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ARGON, A NEW CONSTITUENT OF THE ATMOSPHERE.[1]

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I. *Density of Nitrogen from Various Sources.*

In a former paper[2] it has been shown that nitrogen extracted from chemical compounds is about 0.5 per cent. lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows:

From nitric oxide.....	2.3001
From nitrous oxide.....	2.2990
From ammonium nitrite...	2.2987

while for "atmospheric nitrogen" there was found—

By hot copper (1892).....	2.3103
By hot iron (1893).....	2.3100
By ferrous hydrate (1894).	2.3102

At the suggestion of Professor Thorpe experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The hypobromite was pre-

[1] An abstract of the paper read before the Royal Society at the meeting held January 31, 1895. Communicated by the authors for publication in this Journal.

[2] Rayleigh: On an Anomaly encountered in Determinations of the Density of Nitrogen Gas, Proc. Roy. Soc., **55**, 340 (1894).

pared from commercial materials in the proportions recommended for the analysis of urea. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were, in a great degree, obviated by passing the gas over hot metals. For the fillings of June 6, 9, and 13 the gas passed through a short length of tube containing copper in the form of fine wire heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The mean result, reduced so as to correspond with those above quoted, is 2.2985.

Without using heat, it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air simply bubbled through the hypobromite solution, is allowed to pass with constant shaking over mercury contained in a U tube, the surface of the metal was soon fouled.

Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The mean result from three fillings is 2.2987.

It will be seen that, in spite of the slight nitrous smell, there is no appreciable difference in the densities of gas pre-

pared from ammonium nitrite with and without the treatment by hot metals. The result is interesting as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:

From nitric oxide	2.3001
From nitrous oxide	2.2990
From ammonium nitrite purified at a red heat	2.2987
From urea	2.2985
From ammonium nitrite purified in the cold	2.2987
Mean	2.2990

These numbers, as well as those above quoted for "atmospheric nitrogen," are subject to a deduction of 0.0006 for the shrinkage of the globe when exhausted.[1] If they are then multiplied in the ratio of 2.3108 : 1.2572, they will express the weights of the gas in grams per liter. Thus, as regards the mean numbers, we find as the weight per liter under standard conditions of chemical nitrogen 1.2505, that of atmospheric nitrogen being 1.2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2.2984 : 2.6276 = 0.87471$; so that if $O_2 = 16$, $N_2 = 13.9954$. Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14; but if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

To the above list may be added nitrogen prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride and afterwards liberated in the free state by means of calcium hypochlorite. The purification

[1] Rayleigh: On the Densities of the Principal Gases, Proc. Roy. Soc., **53**, 134 (1893).

was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:

Globe empty, Oct. 30, Nov. 5.....	2.82313
Globe full, Oct. 31.....	0.52395
Weight of gas.....	2.29918

It differs inappreciably from the mean of other results; *viz.*, 2.2990, and is of special interest as relating to gas which, at one stage of its history, formed part of the atmosphere.

Another determination, with a different apparatus, of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated by degrees, the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly-prepared solution of sodium hypobromite. The nitrogen was collected in a gas-holder over water which had previously been boiled, so as, at all events partially to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18.38° and 754.4 mm. pressure, 162.843 cc. of this nitrogen weighed 0.18963 gram. Hence,

Weight of 1 liter at 0° and 760 mm. pressure = 1.2521 gram.

The mean result of the weight of 1 liter of "chemical" nitrogen has been found to equal 1.2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia produced from the magnesium nitride is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose the ammo-

nia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardized by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 cc. precipitated the chlorine from 0.001701 gram of ammonium chloride.

1. Ammonium chloride from orange-colored sample of magnesium nitride contained 66.35 per cent. of chlorine.

2. Ammonium chloride from blackish magnesium nitride contained 66.35 per cent. of chlorine.

3. Ammonium chloride from nitride containing a large amount of unattacked magnesium contained 66.30 per cent. of chlorine.

Taking for the atomic weights of hydrogen H = 1.0032, of nitrogen N = 14.04, and of chlorine Cl = 35.46, the theoretical amount of chlorine in ammonium chloride is 66.27 per cent.

From these results—that nitrogen prepared from magnesium nitride, obtained by passing "atmospheric" nitrogen over red-hot magnesium has the density of "chemical" nitrogen, and that ammonium chloride, prepared from magnesium nitride, contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen.

II. *Reasons for Suspecting a Hitherto Undiscovered Constituent in Air.*

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these, the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot cupric oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity. At this stage it

seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behavior of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance their life would probably be short. On standing they might be expected to disappear, in partial analogy with the known behavior of ozone. With this idea in view, a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first.[1]

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, 0.5 per cent. only by volume would be needed; or, if the density were but half as much again as that of nitrogen, then 1 per cent. would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

[1] Proc. Roy. Soc., **55**, 344, 1894.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. This experiment, although in view from the first, was not executed until a later stage of the inquiry (VI), when results were obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we, therefore, turned our attention, in the first instance, to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favor of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid, is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U tube.[1]

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmos-

[1] Experiments on Air: Phil. Trans., **75**, 372, 1785.

phere, than that it is not diminished by lime-water, caustic alkalies, or nitrous air; that it is unfit to support fire, or maintain life in animals; and that its specific gravity is not much less than that of common air; so that though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reasonable to suppose, that part, at least, of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not, in reality, many different substances compounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest, which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place. Having, by these means, condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air, after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of

the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data[1] from which it is possible to determine the rate of absorption of the mixed gases in his experiment. This was about 1 cc. per hour, of which two-fifths would be nitrogen.

III. *Methods of Causing Free Nitrogen to Combine.*

To eliminate nitrogen from air, in order to ascertain whether any other gas could be detected, involves the use of some absorbent. The elements which have been found to combine directly with nitrogen are boron, silicon, titanium, lithium, strontium, barium, magnesium, aluminium, mercury, and, under the influence of an electric discharge, hydrogen in presence of acid, and oxygen in presence of alkali. Besides these, a mixture of barium carbonate and carbon at a high temperature is known to be effective. Of those tried, magnesium, in the form of turnings, was found to be the best. When nitrogen is passed over magnesium, heated in a tube of hard glass to bright redness, combustion with incandescence begins at the end of the tube through which the gas is introduced, and proceeds regularly until all the metal has been converted into nitride. Between 7 and 8 liters of nitrogen can be absorbed in a single tube; the nitride formed is a porous, dirty orange-colored substance.

IV. *Early Experiments on Sparking Nitrogen with Oxygen in Presence of Alkali.*

In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by ∪-shaped glass tubes passing through the liquid round the mouth of the test-tube. With the given battery and coil a somewhat short spark or arc of about 5 mm. was found to be more favorable than a longer one. When the mixed gases were in the right proportion the rate of absorption was about

[1] Phil. Trans., **78**, 271 (1788).

30 cc. per hour, or 30 times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 cc. of air. To this, oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury, in which the volume was found to be 1 cc. On treatment with alkaline pyrogallate, the gas shrank to 0.32 cc. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favorable proportion.

The residue was then transferred to the test-tube with an addition of another 50 cc. of air, and the whole worked up with oxygen as before. The residue was now 2.2 cc., and, after removal of oxygen, 0.76 cc.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapor) was unduly high. But any doubts that were felt upon this score were removed by comparison-experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 cc. of air with 7 cc. of oxygen was sparked for one and one-fourth hours, the residue was 0.47 cc., and after removal of oxygen 0.06 cc. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidized could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a com-

parison with the air spectrum, taken under similar conditions, proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

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V. *Early Experiments on Withdrawal of Nitrogen from Air by Means of Red-hot Magnesium.*

A preliminary experiment carried out by Mr. Percy Williams on the absorption of atmospheric nitrogen, freed from oxygen by means of red-hot copper, in which the gas was not passed over, but simply allowed to remain in contact with the metal, gave a residue of density 14.88. This result, although not conclusive, was encouraging; and an attempt was made, on a larger scale, by passing atmospheric nitrogen backwards and forwards over red-hot magnesium from one large gas-holder to another to obtain a considerable quantity of the heavier gas. In the course of ten days, about 1,500 cc. were collected and transferred gradually to a mercury gas-holder, from which the gas was passed over soda-lime, phosphoric anhydride, magnesium at a red heat, copper oxide, soda-lime, and phosphoric anhydride into a second mercury gas-holder. After some days the gas was reduced in volume to about 200 cc., and its density was found to be 16.1. After further absorption, in which the volume was still further reduced, the density of the residue was increased to 19.09.

On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen, the density of the remaining gas was calculated to be 20.0.

The spectrum of the gas of density 19.09, though showing nitrogen bands, showed many other lines which were not recognizable as belonging to any known element.

VI. *Proof of the Presence of Argon in Air by Means of Atmolysis.*

It has already (II) been suggested that if "atmospheric nitrogen" contain two gases of different densities, it should

be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyzer was prepared (after Graham) by combining a number of "churchwarden" tobacco-pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water-pump. One end of the combination of pipes was open to the atmosphere; the other end was connected to a bottle-aspirator, initially full of water, and so arranged as to draw about 2 per cent. of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of 2 per cent. was never much exceeded.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper, followed by cupric oxide, ammonia by sulphuric acid, moisture and carbonic acid by potash and phosphoric anhydride.

In a total weight of approximately 2.3 grams the excess of weight of the diffused nitrogen over ordinary atmospheric nitrogen was, in four experiments, 0.0049, 0.0014, 0.0027, 0.0015.

The mean excess of the four determinations is 0.00262 gram, or, if we omit the first, which depended upon a vacuum-weighing of two months old, 0.00187 gram.

The gas from prepared air was thus, in every case, denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share,

and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface, in operation, was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions, in which the excess was I, 0.0037; II, 0.0033.

The excess being larger than before is doubtless due to the greater efficiency of the atmolyzing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture, and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen-apparatus. The advance of 3.5 mgms. on the 11 mgms., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

VII. *Negative Experiments to Prove that Argon is not Derived from Nitrogen from Chemical Sources.*

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (VI), appeared overwhelming, we have thought it undesirable to shrink from any labor that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 liters of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. The gas remaining at the close of the large-scale operations was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 cc.

This was transferred, and, after treatment with alkaline pyrogallate to remove oxygen, measured 3.3 cc. If atmospheric nitrogen had been employed, the final residue should have been about 30 cc. Of the 3.3 cc. actually left, a part is accounted for by an accident, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5,660 cc. of nitrogen from ammonium nitrite were treated with oxygen. The final residue was 3.5 cc., and was found to consist mainly of argon.

The source of the residual argon is to be sought in the water used for the manipulation of the large quantities of gas, (6 liters of nitrogen and 11 liters of oxygen) employed. When carbonic acid was collected in a similar manner and subsequently absorbed by potash, it was found to have acquired a contamination consistent with this explanation.

Negative experiments were also carried out absorbing nitrogen by means of magnesium. In one instance 3 liters of nitrogen prepared from ammonium chloride and bleaching-powder, were reduced in volume to 4.5 cc., and on sparking with oxygen its volume was further reduced to about 3 cc. The residue appeared to consist of argon. Another experiment, in which 15 liters of nitrogen from ammonium nitrite were absorbed, gave a final residue of 3.5 cc. Atmospheric nitrogen, in the latter case, would have yielded 150 cc., hence less than $\frac{1}{40}$ of the normal quantity was obtained. It should be mentioned that leakage occurred at one stage, by which perhaps 200 cc. of air entered the apparatus; and, besides, the nitrogen was collected over water from which it doubtless acquired some argon. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

VIII. *Separation of Argon on a Large Scale.*

To prepare argon on a large scale air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion-tube, heated in a furnace, and containing copper, in order to remove all traces of oxy-

gen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion tube packed tightly with magnesium turnings, and heated to redness in a second furnace. From this tube it passes through a second index tube, and enters a small gas-holder capable of containing 3 or 4 liters. A single tube of magnesium will absorb from 7 to 8 liters of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 or 150 liters of atmospheric nitrogen, which may amount to 4 or 5 liters, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 cc. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume, it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube no gas may be lost. Before ceasing to heat, the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high-tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.[1] The plant consists of a De Meritens alternator, actuated by a gas-engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is 3 liters per hour, about 3,000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7,925 cc., and of oxygen (prepared from chlorate of potash), 9,137 cc. On the eighth and ninth days oxygen alone was added, of which about 500 cc. were consumed, while there remained about 700 cc. in the flask. Hence the proportion in which the air and oxygen combined was as 79 : 96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc-discharge changes greatly in appearance, becoming narrower and blue rather than greenish in color.

The final treatment of the residual 700 cc. of gas was on the model of the small-scale operations already described. Oxygen or hydrogen could be supplied at pleasure from an electrolytic apparatus, but in no way could the volume be reduced below 65 cc. This residue refused oxidation, and showed no trace of the yellow line of nitrogen, even under favorable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hours' spark-

[1] Chem. News, **65**, 301, 1892.

ing with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about 1.5 per cent. was clearly, and about 3 per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

IX. *Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidized except nitrogen. Thus, if

D = density of chemical nitrogen,
D' = " " atmospheric nitrogen,
d = " " argon,
α = proportional volume of argon in atmospheric nitrogen,

the law of mixtures gives

$$\alpha d + (1-\alpha)D = D',$$

or

$$d = D + (D'-D)/\alpha.$$

In this formula $D'-D$ and α are both small, but they are known with fair accuracy. From the data already given

$$\alpha = \frac{65}{0.79 \times 7925},$$

whence if (on an arbitrary scale of reckoning) $D = 2.2990$, $D' = 2.3102$, we find $d = 3.378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20.6.

A direct determination by weighing is desirable, but, hitherto, it has not been feasible to collect, by this means, sufficient to fill the large globe employed for other gases. A *mixture* of about 400 cc. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen; *viz.*, 2.6270. Thus, if α be the ratio of the volume of argon to the whole volume, the number for argon will be

$$2.6270 + 0.1045/\alpha.$$

The value of α, being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $\alpha = 0.1845$; whence for the weight of the gas we get 3.193, so that, if $O_2 = 16$, the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.

X. *Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19.09; and, after sparking with oxygen, it was calculated to be 20.0. The most reliable results of a number of determinations give it as 19.90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19.90 showed no spectrum of nitrogen when examined in a vacuum-tube. It is right, however, to remark that the highest density registered was 20.38. But there is some reason here to distrust the weighing of the vacuous globe.

XI. *Spectrum of Argon.*

The spectrum of argon, seen in a vacuum-tube of about 3 mm. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696.56 and 705.64, 10^{-6} mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue or blue-violet line of wave-length 470.2; and last, in the

less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar-discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most characteristic lines are, perhaps, those in the neighborhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapor. The approximate wave-lengths are

487.91	Strong.
[486.07]	F.
484.71	Not quite so strong.
480.52	Strong.
476.50	Fairly strong characteristic triplet.
473.53	
472.56	

It is necessary to anticipate Mr. Crookes' communication, and to state that when the current is passed from the induction-coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,[1] who has noticed a similar phenomenon, attributes it to the presence of two gases. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is, in reality, a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears,

[1] Proc. Phys. Soc., 1893, p. 147.

and the argon spectrum manifests itself in full purity. A specially constructed tube, with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic-soda solution.

Professor Schuster also has found the principal lines identical in the spectra of the two gases, as observed by the jar-discharge at atmospheric pressure.

XII. *Solubility of Argon in Water.*

Determinations of the solubility, in water, of argon prepared by sparking, gave 3.94 volumes per 100 of water at 12°. The solubility of gas prepared by means of magnesium was found to be 4.05 volumes per 100 at 13.9°. The gas is, therefore, about 2½ times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded in Section I, were 2.3221 and 2.3227, showing an excess of 24 mgms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is 11 mgms., we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbonic acid, whose weight was only about midway between that of true and atmospheric nitrogen.

XIII. *Behavior at Low Temperatures.*[1]

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of —90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical temperature (—121°) and a lower boiling-point (—187°) than oxygen, and that he has succeeded in solidifying argon to white crystals, melting at —189.6°. The density of the liquid is approximately 1.5, that of oxygen being 1.124, and of nitrogen 0.885. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum-tube.

XIV. *Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation

$$n\lambda = v = \sqrt{\left\{ \frac{e}{d}(1+\alpha t)\frac{C_p}{C_v} \right\}},$$

when n is the frequency, λ the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1+\alpha t)$ the temperature correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound, many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion

$$\lambda^2 d : \lambda'^2 d' :: 1.41 : x,$$

[1] The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

where, for example, λ and d refer to air, of which the ratio is 1.41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about 2 mm. diameter, and one in one of 8 mm., made with entirely different samples of gas, gave, the first, 1.65 as the ratio, and the second, 1.61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1.276, instead of 1.288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73.6, instead of 74.5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1.39, instead of 1.402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, *viz.*, 1.66, proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.[1]

XV. *Attempts to Induce Chemical Combination.*

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here, that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali, also when sparked; nor with chlorine dry or moist, when sparked; nor with phosphorus at a bright-red heat, nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic lustre remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum black does not absorb it, nor does platinum sponge; and wet oxidizing and chlorinating agents, such as nitro-hydrochloric acid, bromine-water, bromine and alkali, and

[1] Kundt and Warburg: Ann. der Phys. Pogg., **138**, 337, 527.

hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica, and of sodium and boracic anhydride, are also without action; hence, it appears to resist attack by nascent silicon and by nascent boron.

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XVI. *General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mixture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence.

First. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density 20, compared with hydrogen, "atmospheric" nitrogen should contain of it approximately 1 per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

Second. This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

Third. As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

Fourth. It is in the highest degree improbable that two processes, so different from each other, should manufacture

the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence argon cannot have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then

$$\frac{K}{H}=\frac{3(C_p-C_v)}{2C_v},$$

C_p and C_v denoting, as usual, the specific heat at constant pressure and at constant volume, respectively. Hence if, as for mercury-vapor and for argon (XIV), the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that $K=H$, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapor, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture

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of elements; and hence it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be 40.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes' observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling, that in our future experimental work we shall endeavor to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have therefore to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are

Chlorine	35.5
Potassium	39.1
Calcium	40.0
Scandium	44.0

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in

almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85.5, *viz.*, 82, the mixture should consist of 93.3 per cent. of the lighter, and 6.7 per cent. of the heavier element. But it appears improbable that such a high percentage as 6.7 of a heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contain

$$Si_n^{IV}, \quad P_4^{III \text{ and } V}, \quad S_{8 \text{ to } 2}^{II \text{ to } VI}, \quad \text{and} \quad Cl_2^{I \text{ to } VII},$$

might be expected to end with an element of monatomic molecules, of no valency, *i. e.*, incapable of forming a compound, or, if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they, in any way, lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and

comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kellas, and Matthews, who have materially assisted us in the prosecution of this research.

ON THE SPECTRA OF ARGON.[1]

By William Crookes, F.R.S., &c.

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wavelengths, which follows, and on a map of the lines accurately drawn to scale. The map is 40 feet long, and the probable error of position of any line on it is not greater than 1 mm.

Argon resembles nitrogen in that it gives two distinct spectra according to the strength of the induction-current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and, however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disap-

[1] Read at the meeting of the Royal Society held January 31, 1895. Communicated for publication in this Journal.

pear when the induction-spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum-tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxyhydrogen blowpipe. I have not yet succeeded in melting platinum or iridioplatinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tin-foil, connected with the terminals of the induction-coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 mm. At this point the color of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation,"[1] and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum-tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the color of the luminous discharge changes from red to a rich steel-blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called, for brevity, red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue color and spectrum entirely free from the red. The red is easily got by using a large coil[2] actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue. The blue color may be obtained with the large coil by actuating it with a current of 3.84 ampères and 11 volts, in-

[1] Proc. Roy. Soc., **50**, 88, June, 1891.

[2] The coil used has about 60 miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove's cells.

tercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue color can be obtained by using 3 Grove's cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that a low electromotive force (3 cm. spark, or 27,600 volts) is required to bring out the red, and a high E.M.F and a very hot spark for the blue. I have occasionally had an argon tube in so sensitive a state, that with the commutator turned one way the color was red, and the other way blue. Induction-coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum-tube also acts as a valve. The red glow is produced by the positive spark and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen. In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all. Of these 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay, I was allowed to take some vacuum-tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest, the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but

the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum-tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 ampères and 11 volts; no jar was interposed. At a pressure of 3 mm. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until, at a pressure of about half a millimeter, flashes of blue light made their appearance. At a quarter of a millimeter the color of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord Rayleigh. He had prepared it from the atmosphere by sparking, and it was considered to contain about 3 per cent. of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 mm. and kept on the pump. At this pressure the nitrogen conducted all the induction-current, and the spectrum showed nothing but the nitrogen bands. The pump was slowly kept going and spectrum observations were continuously taken. When the pressure fell to about 3 mm. a change came over the spectrum; the nitrogen bands disappeared, and the spectrum of argon took its place, the only contamination being a little aqueous vapor, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one showing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor Ramsay. From these it is seen that the spectra given by argon, obtained by totally distinct methods from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,[1] having

[1] When a current of 65 volts and 15 ampères, alternating 130 times a second, is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started, the poles can be drawn asunder till the flame bridges across 212 mm. When the terminals are more than 46 mm. apart, the flame will not strike across. By enclosing this flame in a reservoir over alkaline water and feeding it with air and oxygen I can burn up a liter of air an hour.

60 to 70 per cent. of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 mm., and the tube was then sealed off. The spark from the large coil actuated with a current of 3.84 ampères and 11 volts was then put on, and the spectrum examined continuously. At first it was that of nitrogen bands. In about half an hour the nitrogen began to fade and the argon lines appear, and in a few minutes later the tube was just short of non-conducting. The color of the gas was rich steel-blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires caused much spattering or "electrical evaporation" of the platinum to take place. The pressure also is the one most suitable for that phenomenon. To this I attribute the rapid absorption of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum-tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 mm. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction-current from the large coil for eight hours before any change was noticed. The last time, when photographing its spectrum, difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The color immediately changed from the reddish-yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty, and by employing a very small jar, I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through except by employing a dangerously large current. Whenever a flash passed it was of a deep blue color. Assuming that the atmos-

phere contains 1 per cent. of argon, the 3 mm. of nitrogen originally in the tube would contain 0.03 mm. of argon. After the nitrogen had been absorbed by the spattering platinum this pressure of argon would be near the point of non-conduction.

In all cases, when argon has been obtained in this manner, the spectrum has been that of the blue glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark; partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until, at a pressure of about 3 mm., it is at the greatest, and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of the blue form to increase, till the vacuum approaches a fraction of a millimeter, when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion, that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body, has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum-tubes containing rarefied nitrogen, which show either the fluted band or the sharp line-spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. Plücker, who was the first to observe this occurrence, says:[1] "When Ruhmkorff's small induction-coil was discharged through a spectral tube

[1] On the Spectra of Ignited Gases and Vapors: Plücker and Hittorf, Phil. Trans. **155**, 21 (1865), Part I.

enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of Geissler's exhauster, finally the beautiful red color of the ignited gas became fainter, and passed gradually into an undetermined violet. When analyzed by the prism, Hα (the red, C, line) disappeared, while Hβ (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

I have prepared tubes containing other gases, as well as nitrogen at different pressures, and have examined their spectra both by eye observations and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 531.7, the aurora line at 557.1, and the helium line at 587.5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapor yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it, except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

The Two Spectra of Argon.

Blue. Wave-length.	Intensity.	Red. Wave-length.	Intensity.	
		764.6	2	
		750.6	4	
		737.7	3	
		726.3	2	
		705.64	10	
		696.56	9	
		684.2	2	
		675.4	6	
		666.4	6	
662.8	4			
		640.7	9	
		637.7	2	
		630.2	4	
		628.1	2	
623.2	4			
		621.0	6	
617.3	6	617.3	6	Coincident.
		614.3	2	
612.0	6			
		609.9	4	
		605.6	2	
		604.5	3	
603.8	8	603.8	8	Coincident.
		593.5	1	
592.6	4	592.6	4	Coincident.
		590.9	6	
		588.7	6	
		585.8	4	
		583.4	2	
		580.3	1	
		577.1	2	
		574.6	6	
		568.3	2	
		565.1	9	
		561.0	9	
		556.7	2	
		555.7	10	
		552.0	1	
		550.1	2	
		549.65	8	
		545.6	6	
		544.4	2	

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
		542.1	4	
		525.8	6	
		522.2	7	
		518.58	10	
		516.5	9	
514.0	10			
506.5	10	506.5	4	Coincident.
501.2	2	501.2	4	Coincident.
500.7	9			
496.55	9	496.55	4	Coincident.
493.8	10	493.8	2	Coincident.
487.9	10	487.9	4	Coincident.
484.75	1			
480.50	7			
476.30	1			
473.45	6			
472.66	2			
		470.12	8	
465.65	5			
		462.95	5	
460.80	8			
		459.45	2	
458.69	6			
457.95	6			
454.35	7			
		451.40	2	
450.95	8	450.95	9	Coincident.
447.83	6			
442.65	10			
442.25	10			
439.95	10			
437.65	9			
436.90	9			
434.85	10			
		434.50	5	
433.35	9	433.35	9	Coincident.
		430.05	9	
429.90	9			
427.70	3			
427.20	7	427.20	8	Coincident.
426.60	6	426.60	4	Coincident.
425.95	8	425.95	9	Coincident.
425.15	2	425.15	3	Coincident.
422.85	6			
420.10	10	420.10	10	Coincident.

Blue. Wave-length.	Intensity.	Red. Wave-length.	Intensity.	
419.80	9	419.80	9	Coincident.
419.15	9	419.15	9	Coincident.
418.30	8	418.30	8	Coincident.
416.45	8	416.45	4	Coincident.
415.95	10	415.95	10	Coincident.
		415.65	6	
413.15	3			
410.50	8			
407.25	8			
404.40	8	404.40	9	Coincident.
403.30	1			
401.30	8			
397.85	1			
396.78	3			
394.85	9	394.85	10	Coincident.
394.35	3			
393.18	3			
392.85	9			
392.75	3			
391.50	1			
		390.45	8	
389.20	5			
387.55	2			
387.18	2			
386.85	8			
385.15	10			
384.55	1			
383.55	2	383.55	3	Coincident.
382.75	2			
380.95	4			
380.35	1			
379.95	1			
378.08	9			
		377.15	1	
377.05	2			
376.60	8			
373.85	3			
372.98	10			
371.80	4			
		363.25	2	
363.17	1			
		362.37	1	
		362.28	1	
361.75	2			
360.50	3	360.50	5	Coincident.
358.70	10			

Blue. Wave-length.	Intensity.	Red. Wave-length.	Intensity.	
358.03	9			
357.50	9			
356.65	2	356.65	4	Coincident.
356.40	2			
		356.28	1	
356.00	2			
355.82	7			
355.45	4	355.45	6	Coincident.
354.75	4			
354.45	7			
353.43	4			
352.05	3			
351.92	4			
351.35	6			
350.88	4			
349.00	10			
347.57	7			
345.35	1			
338.80	1			
309.27	5			
308.48	4			
306.47	2			
304.27	3			
299.82	1			
297.86	1			
294.27	2			
292.96	1			
283.02	1			
279.44	2			
273.45	2			
270.72	0.5			
269.30	1			
266.12	2			
265.26	3			
262.95	1			
257.12	2			
256.07	1			
248.49	1			
243.85	2			
224.66	3			

119 lines in the "Blue" Spectrum.
80 lines in the "Red" Spectrum.

199 total lines.
26 lines common to the two spectra.

THE LIQUEFACTION AND SOLIDIFICATION OF ARGON.[1]

By K. Olszewski, *Professor of Chemistry in the University of Cracow.*

Having been furnished by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behavior at low temperatures and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cc. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19.9 (H = 1); and he thought that at the outside it might contain 1 to 2 per cent. of nitrogen, although it showed no nitrogen-spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as of measuring its vapor-pressure at several other low temperatures, while two other series served to determine its boiling and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene

[1] Read by Prof. W. Ramsay at the meeting of the Royal Society held January 31, 1895. Communicated for publication in this Journal.

had comparatively thin walls (not exceeding 1 mm.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury-reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume, in the liquid state, measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of the liquid ethylene had been lowered to —128.6°, the argon easily condensed to a colorless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:

Expt.	Temperature.	Pressure.
1	—121.2°	50.6 atmos.
2	—121.6°	50.6 "
3	—120.5°	50.6 "
4	—121.3°	50.6 "
5	—121.4°	50.6 "
6	—119.8°	50.6 "
7	—121.3°	50.6 "

In all seven determinations the critical pressure was found to be 50.6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6, less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapor-pressures of argon, a tabular record of which is given below, I noticed slight differences of

pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is —121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapor-pressures were recorded:

Expt.	Temperature.	Pressure	Expt.	Temperature.	Pressure.
8	—128.6°	38.0 atmos.	13	—134.4°	29.8 atmos.
9	—129.6°	35.8 "	14	—135.1°	29.0 "
10	—129.4°	35.8 "	15	—136.2°	27.3 "
11	—129.3°	35.8 "	16	—138.3°	25.3 "
12	—129.6°	35.8 "	17	—139.1°	23.7 "

In experiments Nos. 9, 10, and 17 the quantity of liquefied argon was very small, for it filled the tube only to a height of 3—5 mm., and in the other experiments the column of liquid argon was 20 mm. high or more.

Determination of the Boiling- and Freezing-Points.

200 cc. of liquid oxygen, prepared in my large apparatus,[1] was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 cc., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (—182.7°)[2] on admitting argon, no appearance of liquefaction could be noticed, even when compressed by increasing the atmospheric pressure by a quarter. This shows that its boiling-point lies below that of oxygen. But on diminishing

[1] Bulletin international de l'Académie de Cracovie, June, 1890; also Beibl. Ann. der Phys., **15**, 29.

[2] I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1.3° lower than that which I previously recorded.

the temperature of the liquid oxygen below —187°, the liquefaction of the argon became manifest. When liquefaction had taken place, I carefully equalized the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers —186.7°, —186.8°, —187.0°, and —187.3°. The mean is —186.9°, which I consider to be the boiling-point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99.5 cc.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 cc. Hence the density of argon at its boiling-point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point (—187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to —191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers: —189.0°, —190.6°, —189.6°, and —189.4°. The mean of these numbers is —189.6°; and this may be accepted as the melting-point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the following table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, *viz.*, between carbon monoxide and oxygen. Its behavior on liquefaction places it nearest to oxygen, but it differs entirely from oxy-

Name.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing-pressure.	Density of gas.	Density of liquid at boiling-point.	Color of liquid.
		Atmos.			mm.			
Hydrogen (H_2).....	Below −220.0°	20.0	?	?	?	1.0	?	Colorless.
Nitrogen (N_2).....	−146.0°	35.0	−194.4°	−214.0°	60	14.0	0.885	"
Carbonic oxide (CO)	−139.5°	35.5	−190.0°	−207.0°	100	14.0	?	"
Argon (A_1).....	−121.0°	50.6	−187.0°	−189.6°	?	19.9	About 1.5	"
Oxygen (O_2).....	−118.8°	50.8	−182.7°	?	?	16.0	1.124	Bluish.
Nitric oxide (NO)...	− 93.5°	71.2	−153.6°	−167.0°	138	15.0	?	Colorless.
Methane (CH_4).....	− 81.8°	54.9	−164.0°	−185.8°	80	8.0	0.415	"

gen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its simple molecular constitution.

ON THE ATOMIC WEIGHT OF OXYGEN. SYNTHESIS OF WEIGHED QUANTITIES OF WATER FROM WEIGHED QUANTITIES OF HYDROGEN AND OF OXYGEN.

By Edward W. Morley.

Many most valuable contributions to our knowledge of the atomic weight of oxygen have been made within ten years by Rayleigh, by Dittmar and Henderson, and by Scott, in England, by Leduc in France, by Thomsen in Denmark, and by Cooke and Richards, by Keiser, and by Noyes, in this country. My own experiments began many years before I learned that others were at work on the subject; but as no assistance could be afforded me, and as, till after the completion of the experiments described in this paper, the whole expense fell upon me, the progress made was so slow that it often seemed hardly worth while to go on.

The process used by Berzelius and Dulong, and by Dumas was first studied. Perhaps the opinion unfavorable to its precision which was formed may be modified by the experience of others, but until our knowledge of the properties of cupric oxide becomes such that we can easily prepare an oxide free from everything but copper and oxygen, the process can hardly be made capable of satisfactory precision. But it cost a year to come to this decision.

It also cost much time to learn how, with ease and certainty, to prepare hydrogen of sufficient purity. When this was accomplished, the method of weighing the gas directly had to be chosen. Some of my globes had a capacity of 21.5 liters,

so that 1.8 grams of hydrogen could be weighed in one of them. Since the weight of such a globe can be determined with a mean error of less than a tenth of a milligram in a single weighing, the process is not an unpromising one. But while it is easy to prepare pure hydrogen, and easy to weigh it, it is by no means easy to introduce it into the globe without contamination, either by mercurial vapor, from a mercurial air-pump, or by organic vapors from the lubricant of a piston air-pump. The difficulties could be surmounted, if no alternative method were available. But there is a better method, and it is easy.

One method of directly weighing hydrogen is, to weigh a suitable gas-bottle with its drying train, then to generate hydrogen in it by the solution of a metal in an acid or in an alkali, and then weigh again. Some of the forms of apparatus which were tried would permit me to weigh over 4 grams of hydrogen in each experiment. But it was impossible to procure easily a metal which gave pure hydrogen, or hydrogen which could be purified with a simple purifying train. Nothing would answer my purpose except zinc redistilled in a vacuum so as to free it from carbon.

There remained only the costly recourse to the method depending on the use of palladium. Chirikoff seems first to have suggested the use of palladium as a means of purifying hydrogen. I began experimenting with the present investigation in mind in 1883, though on a small scale.

The experiments to be described in this paper consist of twelve syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. The hydrogen was absorbed in 600 grams of palladium ; the oxygen was weighed in two globes, in the form of gas. Full details of the experiments are ready for a publication of the Smithsonian Institution, to which those are referred who care to know the nature of the apparatus used, and to see the quantities determined by the balance or the eudiometer, unmodified by any computation. The present paper is but a brief abstract of one part of that paper, giving the final results of each of the experiments, and such a general description of the apparatus as may be sufficient for many.

Apparatus for Producing and Weighing Water.

The apparatus for producing and weighing water consisted of a thin glass tube some 22 centimeters long and 25 millimeters in diameter, Figure 1. Midway in its length, were inserted two tubes, ending within in two platinum jets parallel to the axis of the tube. Just above these jets were two platinum wires for inflaming the jet of hydrogen or of oxygen. The gases came to the jets through drying tubes filled with phosphorus pentoxide, so that the uncombined gases could enter, but the water produced could not escape, if the apparatus were properly used. The ends of the drying tubes were furnished with ground-joints by which they could be joined to the apparatus for regulating the admission of the gases. The volume of the apparatus was not far from 250 cc., and the weight nearly 100 grams. Before using it, it was exhausted to the ten thousandth of an atmosphere, and closed by fusion. Its volume was determined, and it was then weighed accurately against a counterpoise of the same volume and of 35 or 40 grams greater weight.

FIGURE 1.

Apparatus for Weighing Hydrogen.

My plant for weighing hydrogen contained 600 grams of palladium; in the first and second experiments this was divided between two tubes, but in the rest, it was all in one tube. Some trifling modifications of its form were made after each accident to it; all these are mentioned in the paper to be issued by the Smithsonian Institution. In the final form no stop-cock was used on this tube; but even in those experiments in which the stop-cock was still attached to the tube, it was never used for any purpose except to regulate the current of gas for a moment. A most fruitful source of annoyance, or even of serious error, was avoided by depending solely on fusion for closing this tube. The tube containing

palladium having been connected by fusion to the source of hydrogen shown at Figure 1 in my paper on the "Volumetric Composition of Water,"[1] the palladium was heated, and a current of the gas was passed for half an hour or more. The tube was then closed by fusion, the metal was cooled, and the gas was passed into it to saturation. The tube was then again opened and a current of the gas was passed for two or three hours, so as to remove any nitrogen which might conceivably have accumulated, after which it was closed by fusion at all points, its volume was determined by hydrostatic weighing, and its weight was determined by the method of reversal, using a counterpoise of the same volume and the same weight. The observations of weight were repeated at intervals.

Apparatus for Weighing Oxygen.

The two globes used for weighing oxygen contained 20.0 and 21.5 liters. They were provided with counterpoises which were equal to them in volume when the globes were exhausted, and the expansion of the globes produced by filling them with gas was compensated, the compensation being a simple and accurate method of dispensing with the observations of pressure and temperature which would have been necessary in order to compute corrections for differences of volume. The globes were exhausted with a Toepler pump to one part in thirty or fifty thousand, and filled with pure and dry oxygen. They were weighed as stated before. It was thought that the amount of mercury vapor which contaminated the oxygen was negligible, experiments seeming to justify this opinion. That the oxygen was free from chlorine, although made from potassium chlorate, was proved by suitable examination of the water produced from it.

Balance.

The balance used was made by Becker, of Rotterdam, and carries a kilogram in each pan. It was procured for this investigation, and has been used for nothing else. It was set up in a room of nearly constant temperature, on the stone

[1] Am. Jour. Science, **41**, 225.

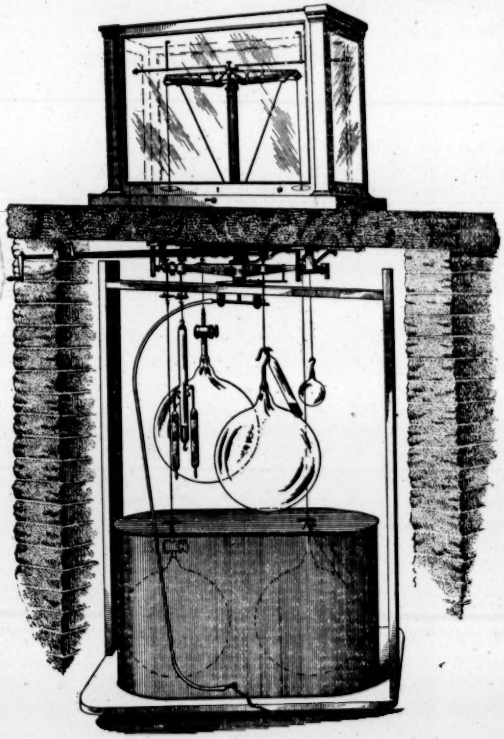


FIGURE 2.

Figure 2 shows the balance and the mechanism for weighing by reversal. The apparatus was photographed while supported temporarily for the purpose, and the drawing made from the photograph as accurately as the artist could well do it, but some details are not quite correct. Hooks attached to the pans of the balance pass down through the stone cover of the vault. Six hooks carrying the globes and other objects are supported by six arms just below the stone. By means of the handles seen well to the left, any one of these six hooks can be engaged in either of the first pair, and then left attached to it, and free from contact with the arm. The current of dry air needed to supply the desiccators was introduced through the axis of the reversal mechanism, as suggested by the rubber tube in the drawing. The desiccators for the second and third pairs of objects are not shown.

cover of a closet or cave of a little more than a meter in each internal dimension. Under the balance, fastened to the under side of this stone cover, is a reversal apparatus by means of which any one of three pairs of objects may be suspended from either pan of the balance without opening the cave or approaching the balance. With this apparatus, objects to be weighed were placed in the cave, each pair in its desiccator, and left in dry air for hours before weighing. After weighing each pair of objects at least four times, by reversal, at intervals of at least half an hour, it was hoped that the weights might be considered fairly determined. The probable errors of the results seem to justify this hope.

Combining the Gases to Produce Water.

When the hydrogen, the oxygen, and the apparatus for containing the water produced, had been weighed, the apparatus was set together. The apparatus for producing water was opened by breaking off the tubes near the ground-joints of the drying tubes, of course taking means to prevent the admission of moisture with the entering air. The apparatus was then connected to the system of stop-cocks and gauges for controlling the admission of the gases. To this same system were then connected the palladium tube and the two globes of oxygen. Before these were opened to admit gases to the system, the combustion apparatus and the system of tubes were exhausted by a Toepler pump which was permanently connected to the apparatus. After the pump was shut off, the gases were admitted to the connecting tubes and into the combustion apparatus itself where they were ignited by sparks between the wires for the purpose. Immersion in water kept this part of the apparatus at a suitable temperature.

After the combustion was ended, the palladium tube and the globes for oxygen were closed, and the water which had been produced was cooled to $-20°$, so as to make the tension of its vapor small. The Toepler pump again exhausted the apparatus, and the gas withdrawn from the globes and the tube of palladium, but remaining unconsumed in the apparatus, was transferred to an eudiometer. The combustion

apparatus was closed by fusion and weighed together with the parts removed in the manipulation of opening and closing it. The same was done with the tube containing palladium, which was also weighed hydrostatically, to detect any change of volume due to heating. When the globes had been weighed, it was known how much had been withdrawn from each source of gas. The unconsumed residue being measured and analyzed, and the proper subtraction being made, it was known how much of each gas had been combined to form water, which gave the ratio sought. From the weight of water produced, compared with the weight of hydrogen used, was obtained a second determination of the ratio.

No rubber joints were used about the apparatus; all connections were made by fusion, except where parts had to have their weight preserved unchanged, when they were connected to adjoining pieces by suitable ground-joints made tight with paraffin.

The results of the twelve experiments made by this method are given in the following table.

Weights of hydrogen, of oxygen, and of water formed, with ratios deduced:

Hydrogen.	Oxygen.	Ratio.	Water.	Ratio.
3.2645	25.9176	15.878	29.1788	17.877
3.2559	25.8531	15.881	29.1052	17.878
3.8193	30.3210	15.878	34.1389	17.873
3.8450	30.5294	15.880	Apparatus broken.	
3.8382	30.4700	15.877	34.3151	17.881
3.8523	30.5818	15.877	34.4327	17.876
3.8297	30.4013	15.877	34.2284	17.875
3.8286	30.3966	15.878	34.2261	17.879
3.8225	30.3497	15.879	34.1742	17.881
3.8220	30.3479	15.881	34.1743	17.883
3.7637	29.8865	15.881	33.6540	17.883
3.8211	30.3429	15.882	34.1559	17.878
Means.....		15.8792 ± 0.00032		17.8785 ± 0.00066

Besides the full details of experiments here briefly described, the paper now in the hands of the Secretary of the Smithsonian Institution contains three series of determinations of the density of oxygen under normal conditions at the sea-level in latitude 45°; two series of similar determinations for hydrogen by the processes hitherto used, which are

rejected for a suspected source of error incident to such determinations; three series of determinations of the density of hydrogen by a new method which avoids the error suspected, which were carried out with two independent apparatus; and a determination of the volumetric composition of water by a process which is, in one respect, similar to that lately used by Leduc. The combination of these quantities gives a third determination of the atomic weight of oxygen, of which the trustworthiness, as far as can be judged from probable errors, is equal to that of any determination hitherto made; and it agrees absurdly well with the two results from the syntheses. In this work on the densities, I have had generous help from Mrs. Amasa Stone, from Messrs. Warner and Swasey, from Mr. C. W. Wason, from the East Cleveland Railroad Company and the succeeding corporation, the Cleveland Electric Railway Company, and from the Smithsonian Institution; which I am glad of the opportunity to acknowledge.

The following table gives the more important results of the work on the densities and volumetric composition, together with the final results of the experiments described in the present paper. To it is appended a table showing the results of previous experimenters, which Professor F. W. Clarke had revised for a forthcoming work, and which he kindly furnished to me:

Density of oxygen, latitude 45°	1.42895 ± 0.000034
Density of hydrogen	0.08987 ± 0.0000027
Ratio of densities	15.9002 ± 0.00061
Volumetric composition of water at 0°.	2.0027 ± 0.00014
Atomic ratio from densities and volumetric ratio	15.879 ± 0.0011[1]
Atomic ratio, syntheses	15.8792 ± 0.00032
Molecular weight of water, syntheses	17.8785 ± 0.00066

Results of other experimenters.	Atomic ratio.
Berzelius and Dulong	15.894 ± 0.057
Dumas	15.961 ± 0.007
Erdmann and Marchand	15.975 ± 0.011
Cooke and Richards	15.869 ± 0.0020
Keiser, 1888	15.951 ± 0.0011
Rayleigh, syntheses	15.89 ± 0.009
Noyes	15.897 ± 0.0017

[1] Atomic ratio, from densities and volumetric ratio by Scott's experiments 15.878.

Results of other experimenters.	Atomic ratio.
Dittmar and Henderson.....	15.867 ±0.0046
Leduc.....	15.881 ±0.013
Morley.....	15.879 ±0.0003

Results of other experimenters.	Ratio of densities.
Regnault, corrected by Crafts.	15.9105±0.0044
Rayleigh, 1888.....	15.884 ±0.0048
" 1892.....	15.882 ±0.0023
Cooke	15.890 ±0.0067
Leduc	15.905 ±0.015
Morley	15.900 ±0.0006

Volumetric composition of water.

Scott.....	2.00285
Morley, eudiometer, (reduced to o°).....	2.0008
Leduc.....	2.0038
" corrected, according to my reduction.	2.0024

While the value 2.0002, which I obtained by direct measurement, is the value which I am certain would be obtained by others working with pure gases in an apparatus of the nature and dimensions used, it is obvious that the result is not a measurement of the quantity desired, but that it is complicated with a phenomenon which is hinted at by the fact that both my own experiments and those of Scott in an apparatus of similar dimensions, yield a result in which the volume of the oxygen comes out too large. But whether I shall have the means of elucidating the supposed cause, remains for the future. I think we may safely trust the values obtained by Scott and by myself in our last determinations ;—

Scott.....	2.00285
Morley.....	2.00270

ON THE CHLORONITRIDES OF PHOSPHORUS.[1]

By H. N. Stokes.

"Chlorophosphuret of nitrogen" (*Chlorphosphorstickstoff*) was discovered in 1832 by Liebig,[2] while attempting to pre-

[1] The following work was begun in the laboratory of the School of Pharmacy, Northwestern University, Chicago, and continued in the laboratory of the United States Geological Survey. I wish to express my sincere thanks to Prof. J. H. Long, of the former institution, for his kindness in permitting me to work in his laboratory, and to Prof. F. W. Clarke, of the Geological Survey, for the opportunity of continuing the investigation.

[2] Liebig-Wöhler, Briefwechsel **1**, 63; Ann. Chem. (Liebig), **11**, 146, (1834).

pare amides of phosphoric acid by acting on phosphorus pentachloride with gaseous ammonia and with ammonium chloride. Analysis[1] led to the formula $P_3N_3Cl_5$, and he observed that the compound could be distilled with steam, or boiled with acids or alkalies without appreciable decomposition—properties unique in a phosphorus-chlorine compound.

Liebig did not pursue the subject much further, but at his suggestion Gladstone[2] in 1849 continued the study of the phosphorus-nitrogen compounds and, incidentally, of chlorophosphuret of nitrogen. In his papers on this body,[3] Gladstone detailed a method of preparation from phosphorus pentachloride and ammonium chloride, and pointed out some of its properties—among them its decomposition in aqueous ether or by alcoholic alkalies, into hydrochloric acid and a nitrogenous compound, deutazophosphoric acid. Gladstone adopted Liebig's formula, $P_3N_2Cl_5$. The correctness of this was disputed on theoretical grounds by Laurent[4] and Gerhardt,[5] and the formula $PNCl_2$, suggested. At a later date, Gladstone and Holmes[6] revised the work of the former, and adopted Laurent and Gerhardt's formula, at the same time showing, on the basis of the vapor-density, that it must be tripled: $P_3N_3Cl_6$.

Later, Wichelhaus[7] confirmed the results of Gladstone and Holmes, and suggested the structural formula

$$\begin{array}{c} NPCl_2 \\ / \quad \backslash \\ Cl_2PN—NPCl_2 \end{array},$$

and A. W. Hofmann[8] and Couldridge[9] added some further observations.

By distilling under diminished pressure the reaction-product of phosphorus pentachloride and ammonia-gas, Besson[10] obtained a substance of the composition $PNCl_2$, which he de-

[1] The part of Wöhler in this investigation seems to have consisted merely in making the analyses for Liebig.
[2] Q. J. Chem. Soc., **2**, 121, (1850).
[3] *Ibid*, **3**, 135, 353; Ann. Chem. (Liebig), **76**, 74; **77**, 314.
[4] Compt. rend., **31**, 356, (1850), and Compt. rend. des Trav. de Chimie, (1850), 387.
[5] Compt. rend. des Trav. de Chimie, (1851), 30; Ann. chim. phys., [3], **18**, 204, note.
[6] J. Chem. Soc., [2], **2**, 225, (1864).
[7] Ber. d. chem. Ges., **3**, 163, (1870).
[8] *Ibid*, **17**, 1910, (1884).
[9] J. Chem. Soc., **53**, 398, (1888).
[10] Compt. rend., **114**, 1264, 1480, (1892).

scribes as "un corps solide donnent par sublimation des cristaux très réfringents fusibles à 106°." The low melting-point would indicate a body other than $P_3N_3Cl_6$ (melting-point 114°), but as the latter is the chief volatile product formed under ordinary circumstances, it may be regarded as an open question whether Besson's compound is identical with Liebig's.

Finally, White[1] and Gilpin[2] observed it as a secondary product of the action of phosphorus pentachloride on acid ammonium orthosulphobenzoate—doubtless originating in the action of the ammonia.

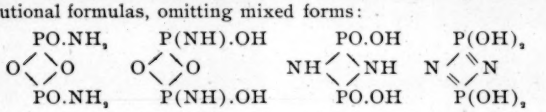
None of these investigations have thrown much light on the constitution of the chlorophosphuret, or on its relation to other phosphorus compounds.

My attention being called to this substance while engaged in studying the amides of phosphoric acid, I have prepared it in large quantity with a view to further investigation. Although the experiments have not progressed far enough to establish any definite constitutional formula, they show that the chlorophosphuret is by no means as intractable as has been supposed, and that it is one of an homologous series of compounds, having the general formula $(PNCl_2)_x$, which are the chlorides of an homologous series of acids, $(PNO_2H_2)_x$, the *metaphosphimic acids*. From the reaction-product of phosphorus pentachloride and ammonium chloride I have thus far isolated the body $(PNCl_2)_4$, which almost equals $(PNCl_2)_3$ in stability, and which yields, on saponification, an acid $(PNO_2H_2)_4$, also an extremely stable substance. A further product of the reaction is a stable, oily chloride $(PNCl_2)_x$ of high, but as yet unknown, molecular weight. I have also obtained from Liebig's chlorophosphuret the corresponding acid $(PNO_2H_2)_3$, an intermediate chlorhydrine $P_3N_3Cl_4O_2H_2$, and a chloramide $P_3N_3Cl_4(NH_2)_2$. The object of the present paper is mainly to describe the preparation and properties of the chlorides, the consideration of the acids being deferred to a later occasion.

Nomenclature.—In view of the large number of phosphorus-nitrogen compounds actually known or theoretically possible, it is desirable to have a more definite nomenclature than has thus far been used. I have proposed[3] to reserve the name

[1] Dissertation, Baltimore: 1891, p. 13. [2] Dissertation, Baltimore: 1892, pp. 7, 16.
[3] This Journal, **16**, 124, note.

amido-orthophosphoric acid for the ortho-acid, in which one hydroxyl is replaced by the amido group, and to call the isomeric form, $P(NH)(OH)_2$, *orthophosphimic* acid. By analogy an acid $P(NH)\begin{matrix}=O\\ \diagdown OH\end{matrix}$ might be named *metaphosphimic* acid. Corresponding to the polymeric metaphosphoric acids, we may imagine an homologous series of metaphosphimic acids, but for each of these, several forms would be possible, according as the polymerization is effected by means of oxygen or of nitrogen atoms, assuming them to be otherwise built on the same general type. For example, an acid of the formula $P_2N_2O_4H_4$, with cyclic structure, might have any of the following constitutional formulas, omitting mixed forms:



(*a*) Dimetaphosphoryl amide. (*b*) —— (*c*) Dimetaphosphimic acid. (*d*) Diphosphonitrilic acid.

(*a*) and (*b*) represent the amide of a dimetaphosphoric acid with its desmotropic form; (*c*) and (*d*) represent the two forms of an acid isomeric with the former, but not directly derivable from a dimetaphosphoric acid. In the former class, phosphorus is united by means of oxygen; in the latter, by nitrogen. (*b*) and (*c*) are polymers of (PO)(NH)(OH) while (*d*) is a polymer of an acid $N{\equiv}P(OH)_2$, which we may call *phosphonitrilic* acid. Acids of the type (*c*) I call *x*-metaphosphimic acids, and those of the type (*d*), *x*-phosphonitrilic acids.[1]

In the chlorides $P_3N_3Cl_6$ and $P_4N_4Cl_8$, phosphorus must be united by means of nitrogen[2] (in the absence of oxygen); hence also in all probability in the acids derived from them. The direct replacement of chlorine by hydroxyl would result in phosphonitrilic acids, but as the type (*c*) is equally plausible, in the absence of definite experimental grounds, I call them provisionally, metaphosphimic acids. For the chlorides

[1] *x* = mono-, di-, tri-, etc.

[2] Unless we assume P to be joined to P, and N to N, a view which is not supported by their general behavior.

themselves, instead of the old term chlorophosphuret of nitrogen, which is no longer characteristic, the more definite names *tri-* and *tetraphosphonitrilic chloride* may be used.

Experimental Part.

Preparation of the Chlorides.—The theoretical yield of triphosphonitrilic chloride is 55.5 per cent. of the phosphorus pentachloride; in reality, it falls far below this, no matter what process may be employed, and at best is but a by-product. Gladstone[1] states the yield as about 6 per cent. of the pentachloride (11 per cent. of the theoretical), when 1 molecular weight is distilled with 8 molecular weights ammonium chloride. Couldridge[2] obtained, by a similar method, a maximum yield of 10 per cent. of the pentachloride (18 per cent. of the theoretical). As a large excess of ammonium chloride is used, much "phospham" is formed. A modification by Gladstone and Holmes,[3] consisting in acting on the pentachloride with mercuric chloramide, gave no better results.

I made numerous experiments in sealed tubes, at 200–260°, using sal-ammoniac and pentachloride in theoretical proportions. In this case there is no formation of phospham, but the yield of the desired body is not increased—in fact, seems to be even less than by distilling with an excess of ammonium chloride from an open retort. What results, is a mixture of chloronitrides, largely crystalline, but of very various degrees of solubility and stability towards water, of which but a very small portion is volatile with steam. A study of this mixture would, in all probability, lead to the discovery of other members of the series $(PNCl_2)_x$.

I finally adopted a slight modification of Gladstone's original method: A mixture (which need not be very intimate) of 1 part pentachloride and 2 parts dry ammonium chloride is rapidly heated in a tubulated retort (one-third filled) fitted to a receiver containing water, which is connected with one or two Woulff's bottles, with water, to condense the small portions carried over with the escaping hydrochloric acid. The water in the receiver should be gently agitated occasionally, in order to break up the crust forming on the surface. When

[1] Q. J. Chem. Soc., **3**, 135; Ann. Chem. (Liebig), **76**, 76.
[2] J. Chem. Soc., **53**, 399. [3] *Ibid*, [2], **2**, 227.

the decomposition is about half finished, the heating is interrupted and the hard cake of phospham and sal-ammoniac turned over with a rod inserted through the tubulure; this is necessary as it is so poor a conductor that the bottom of the retort melts before the upper portions of the cake are affected. Heating must not be continued too long, because the subliming ammonium chloride acts on the chlorides condensed in the neck of the retort. After cooling, the substances condensed in the neck are removed by scraping and injecting hot water through the tubulure. The yield varies considerably, according to the quantity of mixture taken; the less the amount, the greater the yield. I have obtained as high as 11.5 per cent. Practically it is not desirable to push this too far, and I have obtained the most satisfactory results by distilling 200 grams of mixture at a time. The proportion of ammonium chloride should not be less than 2 parts, otherwise much pentachloride sublimes unchanged. The distillate, after washing with water, is by no means pure triphosphonitrilic chloride; it is a mixture of chlorides, of which about one-half is quite stable towards cold water, but decomposed on distilling with steam. During this operation, nearly all the triphosphonitrilic chloride, $P_3N_3Cl_6$, is deposited as a hard crust in the condenser. Distillation is continued only as long as much substance passes over; during the later stages, large needles—mainly the new chloride, $P_4N_4Cl_8$—slowly collect in the condenser. There remain in the flask, besides a strongly acid liquid, a little solid material, consisting partly of phospham, partly of the crystalline acid ammonium tetrametaphosphimate, $P_4N_4O_8H_6(NH_4)_2$, and a considerable amount of oil which solidifies, on cooling, to a crystalline cake of the compound $P_4N_4Cl_6$, impregnated with an oil of the same empirical composition.

The distillate, consisting of triphosphonitrilic chloride, mixed with about 5 per cent. of tetraphosphonitrilic chloride, is dried, and an approximate separation effected by systematic recrystallization from benzene. This solvent has proved the most satisfactory, because the chlorides, in benzene solution, are scarcely affected by water, and no care need be taken to exclude it completely; aqueous ether, on the contrary, acts with considerable ease. The triphosphonitrilic chloride is pure after three or four recrystallizations, the tetraphosphonitrilic

chloride accumulating in the mother-liquors, the residues from which are again subjected to distillation with steam, the substance remaining in the flask being added to the first residue.

Apart from its influence on the melting-point, the presence of very small quantities of the new body in the triphosphonitrilic chloride is readily detected by dissolving in alcohol-free ether and agitating for several hours with a little water, the tetraphosphonitrilic chloride, being indicated by the formation, in the water, of microscopic needles of the difficultly soluble tetrametaphosphimic acid.

The residue from the distillation with steam is sucked out, whereby most of the oily chloride runs through with the water and may be collected. The substance is then dried, the tetraphosphonitrilic chloride, extracted with benzene and purified by several recrystallizations from this solvent. The residue left by the benzene, treated with dilute ammonia, leaves amorphous substances, and gives up tetrametaphosphimic acid, which is thrown down, on acidifying, as its acid ammonium salt. It may be mentioned here that the affinity of this acid for ammonia is such that its acid salt remains undecomposed even in large excess of hot 10 per cent. nitric acid.

The yield of pure chlorides (from 9 kgms. of phosphorus pentachloride) was $P_3N_3Cl_6$, 6.9 per cent. of the pentachloride, $P_4N_4Cl_8$, 0.76 per cent. of the pentachloride, of which 0.42 per cent. was obtained from the residue and 0.34 per cent. from the crude steam-distillate; these are respectively 12.4 and 1.4 per cent. of the theoretical. A further small amount of tetraphosphonitrilic chloride was decomposed during distillation and, in part, recovered as tetrametaphosphimic acid. The yield of oily chloride was not determined, but it was approximately 1 per cent. of the pentachloride.

It is not easy to give a reason for the relatively much higher yield of the triple phosphonitrilic chloride. Doubtless, more of the quadruple compound is formed than is actually obtained, which, because of its less volatility, fails to distill over before it is attacked by the ammonium chloride, and I have also mentioned the simultaneous formation of large quantities of chlorides, unacted on by cold, but decomposed by boiling water. Still, it seems that there is some cause leading to the

predominant formation and greater stability of this body, perhaps analogous to that acting in the case of the aromatic hydrocarbons. The proof that $P_3N_3Cl_6$ is a cyclic compound has not been found, but the occurrence of the number 6 in each case (C_6 and P_3N_3) is possibly more than a mere coincidence. Tetraphosphonitrilic chloride is also possessed of great stability, but I have observed, in various connections, that its chlorine is less firmly held than in the triple compound. The reverse appears to be true of the derived acids, $P_4N_4O_2H_8$ being more stable than $P_3N_3O_6H_6$.

Analytical Methods.—The analysis of these bodies presents no difficulty. The chlorides, which volatilize on heating, are gently warmed with dilute alcoholic soda or potash. In this solution, chlorine is directly determined as silver chloride; phosphorus is determined after evaporating off the alcohol, either by fusing the residue with sodium carbonate or by boiling for one or two hours with strong sulphuric acid, either of which converts it wholly into phosphoric acid. Nitrogen is determined as ammonia after acidifying the saponification product with hydrochloric acid, evaporating the alcohol and boiling the residue with strong sulphuric acid. Experiment showed that no ammonia is evolved during saponification. In the case of the acids and other non-volatile derivatives, the alcoholic saponification is omitted and the substance decomposed either by boiling with concentrated sulphuric acid, or fusing with sodium carbonate, the precaution being taken in the latter case first to moisten the mixture in the crucible. Owing to the strong reducing action of the imido group at high temperatures, these substances cannot be fused alone in platinum without risk to the crucible. This is true even of the salts, which should give pyro- or metaphosphates, on ignition.

The Chlorides.—As *triphosphonitrilic chloride* has been the object of previous investigation, and as I have begun several lines of investigation with the object of explaining its nature and relations, I state here only a few incidental observations.

This chloride, as was early observed, has great crystallizing power. The rhombic crystals have been measured by Miller[1] and by Groth.[2] When pure it tends to form large thick prisms. I have obtained these (from benzene) as much as 8

[1] J. Chem. Soc., [2], **2**, 227. [2] Ber. d. chem. Ges., **3**, 166.

cm. long and 2 cm. wide, their further growth being hindered only by the size of the flask. When impure, it tends to form rhombic or six-sided plates. It fuses at 114° (corr.), while the quadruple chloride, $P_4N_4Cl_4$, fuses at 123.5° (corr.), but a mixture of equal parts is liquid below 90°. The corrected boiling-point is 256.5° at 760 mm. pressure. Besides the solvents elsewhere mentioned (for some of which quantitative data are given below), warm glacial acetic acid dissolves it readily. On boiling this solution with zinc dust, some phosphuretted hydrogen is evolved. Hot concentrated sulphuric acid dissolves it easily. On boiling, some is decomposed, but the greater part distills off unaltered. The rather pleasant aromatic odor of its vapor has long been known. Although this is by no means irritating, inhaling it in any considerable amount is likely to be followed in two or three hours by alarming difficulty in breathing, succeeded by persistent irritation of the air passages. This insidious property renders care necessary in working with it in large quantities or for extended periods, all the more, as the nose is the best instrument for detecting it.

A vapor-density determination by Victor Meyer's method at 360° in dry hydrogen gave 12.35 (calculated 12.01). The volatilization is complete, but on long boiling in air a little solid substance is deposited. Ethyl bromide and sodium are without action on the ethereal solution. Brombenzene and sodium act slowly on the ether or benzene solution, forming a mixture of brownish amorphous organic substances, in part soluble, in part insoluble in ether, in which only a portion of the chlorine is replaced. No smooth reaction could be obtained.

Zinc ethyl, as observed by Couldridge,[1] is without action at ordinary temperature. On heating together in a sealed tube a violent reaction occurs, accompanied by liberation of gas and carbonization. If the zinc ethyl be diluted with 2 vols. benzene, a mixture of complex addition-products is formed on heating, which are left on evaporating as a no longer soluble white vitreous mass, containing zinc, phosphorus, nitrogen, chlorine, and ethyl. This is decomposed by caustic potash, which liberates a mixture of oily bases of a disagreeable sweetish odor, which are for the greater part decomposed on distil-

[1] J. Chem. Soc., **53**, 398.

lation, and which dissolve in cold water, and are thrown out on warming. These are slowly decomposed, on heating, with hydrochloric acid into ammonia and what appear to be highly complex phosphinic acids, containing nitrogen. At 170° considerable quantities of combustible gases, and of mono-, di-, and triethyl phosphine are formed by the action of zinc ethyl, in addition to a small amount of a crystalline basic substance containing nitrogen, and showing much the same properties as the oily substances alluded to. The yield was very minute.

Action of Water on Triphosphonitrilic Chloride.—By decomposing chlorophosphuret of nitrogen with aqueous ether,[1] or with alcoholic alkalies,[2] Gladstone obtained a substance which he named deutazophosphoric acid. He afterwards obtained this in larger quantity by treating phosphorus oxychloride with dry ammonia, and assigned to it the formula

$$O\begin{matrix}/PO(OH)NH_2\\ \backslash PO(OH)NH_2\end{matrix}'$$

and the name pyrophosphodiamic acid. The formation of such an acid can only be due to a deep decomposition of the molecule.

Although unacted on by water alone or by anhydrous ether alone, I have found that a smooth decomposition is easily effected by dissolving the chlorophosphuret in alcohol-free ether, and shaking this solution a long time with water, whereby intimate contact is effected. The final products are hydrochloric acid and an acid in which the chlorine is wholly replaced by oxygen and hydrogen, without further change. I have named this substance, $P_3N_3O_4H_5$, *trimetaphosphimic acid*.[3] If the water contain bases or acetates in solution, the salts are directly obtained. As the acid will be described in a separate paper, I mention here only that it is extremely soluble and totally devoid of crystallizing power, but forms some

[1] Q. J. Chem. Soc., **3**, 135, 354; Ann. Chem. (Liebig), **76**, 79; **77**, 315.

[2] J. Chem. Soc., [2], **2**, 231.

[3] According to Mente, (Ann. Chem. (Liebig), **248**, 241, 244), Gladstone's pyrophosphodiamic acid is really $NH\begin{matrix}PO.OH\\ \diamond\\ PO.OH\end{matrix}NH$, *i. e.*, dimetaphosphimic acid, which has the same empirical composition as trimetaphosphimic acid. Mente did not obtain his acid from triphosphonitrilic chloride, but from phosphorus oxychloride, and it is not clear that it is really identical with Gladstone's acid from chlorophosphuret of nitrogen. The independent existence and stability of the tetra-acid affords a presumption that other members of the series can exist also.

salts of characteristic crystalline form, and has a strong tendency to form double salts, one of these, $P_3N_3O_4H_3NaBa$, giving especially fine crystals.

As intermediate products, chlorhydrines have been observed. Theoretically, five of these are possible, one of which I have isolated; namely,

Triphosphonitrilic-tetrachlorhydrine, $P_3N_3Cl_4O_3H_3$. — 1 part triphosphonitrilic chloride is dissolved in 10 parts alcohol-free ether, and the solution agitated with about one-third its volume of water for six to eight hours, best by means of a small turbine. The water then contains hydrochloric acid and trimetaphosphimic acid, and the ether contains the chlorhydrines and unchanged chloride. The ether is dried over calcium chloride, and the greater part distilled off in the water-bath, the latter portions being removed at ordinary temperature by a current of dry air. The residue consists of unchanged chloride, the chlorhydrine in question, and small quantities of others. The greater part of the chloride is removed by a little benzene, and the residual chlorhydrine well washed with carbon disulphide. The yield depends somewhat on the time the water has acted, but as there is a continuous conversion of chloride into chlorhydrine, and of the latter into trimetaphosphimic acid, the amount present at any one time is not great. Under the above conditions it was about 10 per cent. of the theoretical, fully one-half the chloride being recovered.

Analysis gave:

	Calculated for $P_3N_3Cl_4O_3H_3$.	Found. (1)	(2)	(3)
P	29.94	....	30.00	30.04
N	13.54	....	13.74	....
Cl	45.59	45.38	48.18	48.37

Ratios: (2) P : N : Cl = 3 : 3.03 : 4.20.
(3) P : Cl = 3 : 4.23.

(1), (2), and (3) represent different preparations, (1) having been further purified by recrystallizing from benzene.

The chlorhydrine forms a white sandy powder, consisting of well-defined, microscopic prisms. It is very difficultly soluble in boiling benzene, and is insoluble in benzine and in carbon disulphide. With the latter it shows a peculiar behavior.

Its refractive index is such that it nearly vanishes and apparently dissolves when brought into the disulphide; on decanting the liquid the moist powder shows beautiful iridescence. Alcohol dissolves it easily and in ether it is much more soluble than the original chloride, the presence of a trace of ether vapor causing it to liquefy instantly. Water dissolves it somewhat slowly, but abundantly, the solution containing hydrochloric acid and trimetaphosphimic acid, the latter being left on rapid evaporation on the water-bath or *in vacuo*, as a transparent, easily soluble gummy residue. From the aqueous solution of the chlorhydrine, salts of trimetaphosphimic acid were directly prepared and analyzed. The chlorhydrine is quite stable in the air at ordinary temperature,[1] but on heating at 100° it slowly increases in weight through absorption of moisture, undergoing decomposition with formation of ammonium chloride. It shows no definite melting-point, but, on rapid heating, liquefies imperfectly, gives off hydrochloric acid, and leaves a mixture of amorphous substances of different degrees of solubility in water.

Other chlorhydrines, partly crystalline, appear to be formed simultaneously, but in relatively small amount, and their isolation is attended with difficulties. Whether the two chlorine atoms removed are associated with the same or with different phosphorus atoms remains to be determined.

Triphosphonitrilic Chloramide, $P_3N_3Cl_4(NH_2)_2$.—The tendency to the formation of stable bodies in which one-third of the chlorine is substituted, observed in the case of the chlorhydrine appears if triphosphonitrilic chloride be acted on in ether solution by ammonia. Gaseous ammonia may be used, but this is by no means necessary, aqueous ammonia producing the same result. If the chloride be dissolved in ether and shaken a short time with 10 per cent. ammonia, but one amide appears to be formed. As soon as a few drops of the ether solution leave, on evaporation, a residue completely soluble in hot water, indicating complete transformation of the chloride, it is dried over calcium chloride and allowed to evaporate spontaneously, whereby a substance crystallizing in needles is deposited. The product, which appeared homogeneous on microscopic examination, was directly analyzed.

[1] On keeping for several months, a slight formation of ammonium salts was observed.

	Calculated for $P_3N_3Cl_4(NH_2)_2$.	Found.
P.....	30.12	29.51
N	22.72	21.98
Cl.....	45.86	44.83

Ratio: $P:N:Cl = 3:4.94:3.98$.

The yield was 67 per cent. of the theoretical, some of the chloride having been further decomposed and dissolved by the ammonia.

Triphosphonitrilic chloramide is quite soluble in ether, and less soluble in hot benzene, from which it crystallizes in long tufts of delicate hairs. It is easily soluble in alcohol, and from the concentrated alcoholic solution it is precipitated by water. Its stability towards water is striking; cold water dissolves it slightly, and, on rapid evaporation, even on the water-bath, much is deposited unaltered; it can even be recrystallized from hot water, though with much decomposition, in needles or short prisms. Its stability in aqueous solution is further indicated by the failure of silver nitrate to give a precipitate except on boiling. Aqueous ammonia has but little action in the cold. On heating its aqueous solution, ammonium chloride and a syrupy acid result. Cold dilute acids have no marked solvent action. It gradually undergoes change at ordinary temperature, and rapidly on heating, without fusing, ammonium chloride and an infusible white substance being the products in the latter case.

Couldridge,[1] by acting on fused triphosphonitrilic chloride with gaseous ammonia, obtained a substance which he regarded as phospham. Both Couldridge and A. W. Hofmann[2] express the opinion that phospham has the composition expressed by the formula $P_3N_3(NH)_3$. I regard this as too sweeping. Apart from the fact that its composition varies with the mode of preparation,[3] it is likely that the true phospham is a mixture of an homologous series of imides $(PN.NH)_x$, derivable from the homologous phosphonitrilic chlorides, $(PNCl_2)_x$.

Tetraphosphonitrilic Chloride, $P_4N_4Cl_8$.—The new chlorophosphuret of nitrogen, prepared as above described, gave the following results on analysis:

[1] J. Chem. Soc., **53**, 398. [2] Ber. d. chem. Ges., **17**, 1911.
[3] Salzmann: Ber. d. chem. Ges., **7**, 494.

	Calculated for $P_4N_4Cl_8$.	Found. (1)	Found. (2)
P	26.77	26.89	27.00
N	12.11	12.35	12.36
Cl	61.12	61.17	61.28

Ratios: (1) P : N : Cl = 1 : 1.01 : 1.99.
(2) P : N : Cl = 1 : 1.01 : 1.99.

(1) and (2) represent different preparations.

The vapor-density, determined by Victor Meyer's method, in dry hydrogen at 360°, was:

	Calculated for $P_4N_4Cl_8$.	Found.
Density	16.03	16.20

I am indebted to Mr. B. H. Hite, of the Johns Hopkins University, for a series of determinations of the molecular weight by the ebullioscopic method. The following is his statement of the results:

Solvent: Benzene. Molecular elevation 26.7.

Substance $(PNCl_2)_x$.

Grams solvent.	Grams substance.	Concentration.	Elevation.	Molecular weight found.	Percentage variation from 464.
37.618	1.1620	3.09	0.177°	466	+0.4
37.618	1.4820	3.94	0.227°	463	−0.2
37.987	1.1107	2.92	0.167°	467	+0.7

These results agree well with the quadruple formula.

The following table gives some of the constants compared with those of $P_3N_3Cl_6$.

	$P_3N_3Cl_6$.	$P_4N_4Cl_8$.
Specific gravity	1.98[1]	2.18[2]
Melting-point (Corr.)	114°	123.5°
Boiling-point, (760 mm. pressure; thermometer wholly in vapor)	256.5°	328.5°
100 parts ether at 20° dissolve	46.5	12.3
100 parts benzene at 20° dissolve	57.4	20.9

Tetraphosphonitrilic chloride forms colorless, brittle prisms, not easily wet by water, and therefore having a strong tendency to float. Superficially, these are not always to be distinguished from those of triphosphonitrilic chloride, but in a general way it may be said that they tend to be much smaller, and are to be measured by millimeters rather than centimeters, and that they tend to vary towards an acicular, rather

[1] Gladstone. [2] $d\frac{21}{4}$.

than a tabular form. In alcohol and in benzine it is much less soluble than $P_3N_3Cl_6$. Hot concentrated sulphuric acid dissolves it, and, on boiling, much hydrochloric acid is evolved, but some of the substance sublimes out unchanged. It may be recrystallized from glacial acetic acid; on boiling this solution with zinc dust, a little hydrogen phosphide is given off, and the solution contains ammonia.

It is perceptibly volatile at its fusing-point, its vapor having an odor suggesting, but perceptibly differing from that of triphosphonitrilic chloride and less aromatic. The fused substance solidifies to a mass of nearly parallel needles, while triphosphonitrilic chloride gives transparent plates. As mentioned above, its volatility with steam is comparatively slight. If boiled for some time in contact with air a minute amount of substance is formed which swells enormously to a clear gelatinous mass in benzene. Alcohol converts it slowly into an oily ether, which aqueous ammonia, on warming, saponifies to tetrametaphosphimic acid.

Action of Water on Tetraphosphonitrilic Chloride.—In its chemical behavior it resembles triphosphonitrilic chloride. It is scarcely acted on by boiling water, yet on prolonged boiling, a minute amount of tetrametaphosphimic acid is formed; aqueous fixed alkalies are without perceptible action, while alcoholic alkalies decompose it easily, but the product is mainly something else than tetrametaphosphimic acid.

A smooth decomposition is effected by dissolving in ether and shaking protractedly with water. The first products of this action consist of chlorhydrines, which remain dissolved in the ether, are crystalline, and readily soluble in cold water, from which solution tetrametaphosphimic acid is rapidly deposited in the form of thick needles; the same acid is the final product of the action of water on the ether solution.

The action of water proceeds rather more rapidly than in case of triphosphonitrilic chloride, but many days are required for complete decomposition. The small amount of material, at present in my possession, made it unadvisable to attempt to isolate any of the chlorhydrines, of which seven are theoretically possible.

Tetrametaphosphimic Acid, $P_4N_4O_8H_8 + 2H_2O$, will be described in a separate paper. It may be remarked here pre-

liminarily that it has highly characteristic properties, is highly crystalline, very difficultly soluble in cold water, and much less soluble in dilute acids, that it readily decomposes soluble chlorides, nitrates, and sulphates, and gives three series of salts, in which respectively one-fourth, one-half, and all the hydrogen is replaced by metal; many of these show characteristic forms. The free acid far surpasses the metaphosphoric acids in stability and may be boiled for hours with nitric acid or *aqua regia* without much decomposition.

Tetraphosphonitrilic chloride is readily extracted from its ethereal solution by aqueous ammonia, the ammoniacal solution giving tetrametaphosphimic acid on warming with hydrochloric acid. No clear evidence of the formation of chloramides has yet been observed.

Oily Phosphonitrilic Chloride.—This substance, obtained from the residues as above stated, has not yet been carefully studied; it is possibly a mixture. It is scarcely volatile without decomposition, not volatile with steam, and not acted on by water, except in ethereal solution, when a moderately soluble phosphimic acid is slowly formed, which crystallizes in needles, and decomposes on warming with water into tetrametaphosphimic acid and ammonium phosphate. The analysis gave:

	Calculated for $(PNCl_2)_x$.	Found.
P.....	26.77	26.73
N.....	12.11	12.09
Cl.....	61.12	61.89

Ratio: P : N : Cl = 1 : 1 : 2.03.

U. S. GEOLOGICAL SURVEY, WASHINGTON,
February, 1895.

ON THE SAPONIFICATION OF THE ETHERS OF THE SULPHONIC ACIDS BY ALCOHOLS.

BY J. H. KASTLE AND PAUL MURRILL.

Many observers have doubtless been impressed with the peculiar differences existing between the carbonic and the sulphonic acids. Some of these differences which have been observed to exist, to some of which we believe that attention is here called for the first time, are as follows:

(1) The great difference in the strength of these two classes

of acids—the sulphonic acids being remarkably strong—the carbonic acids weak.

(2) A striking difference in the stability of their acid chlorides. Many of the acid sulphon-chlorides may be boiled with water for some little time without risk of decomposition, whereas the acid chlorides of the carbonic acids decompose with remarkable ease by such treatment.

(3) A difference is observed in the conduct of the amides of these two classes of acids towards water and dilute acids—the sulphonic amides undergoing no decomposition when boiled with a dilute acid, while in this manner the amides of the carbonic acids are readily changed into their acid and an ammonium salt.

(4) Another very striking difference is to be found in the stability and conduct of the ethereal salts of these two kinds of acids towards water and alcohol—the ethereal salts of the carbonic acids being stable and saponifying with difficulty, whereas the ethereal salts of the sulphonic acids are unstable—decomposing largely upon boiling—and are readily saponified in several ways. For example, it has been observed by one of us—Kastle[1]—that, by boiling the diethyl ether of a sulphon-carbonic acid, *viz.*, diethyl-(*p*)-nitrosulphobenzoate, $C_6H_3\begin{cases}\diagup COOC_2H_5\\ SO_2OC_2H_5\\ \diagdown NO_2\end{cases}$, with water or with alcohol, the ethyl sulphonate part of the compound very easily underwent saponification, yielding an acid, $C_6H_3\begin{cases}\diagup COOC_2H_5\\ SO_2OH\\ \diagdown NO_2\end{cases}$, whereas the ethyl carbonate group underwent no alteration.

Since the time of these observations Krafft and Ross[2] have made a study of the methods of preparation of the sulphonic ethers and of their peculiar conduct towards alcohol. These observers have pointed out that ethers (alkyl oxides) are formed as the result of the action of a sulphonic ether and alcohol, and have called attention to the similarity between sulphuric acid and the sulphonic acids in this respect.

$$HO.SO_2.OC_2H_5 + C_2H_5OH = HO.SO_2.OH + C_2H_5O.C_2H_5.$$
$$C_6H_5.SO_2.OC_2H_5 + C_2H_5OH = C_6H_5SO_2OH + C_2H_5O.C_2H_5.$$

[1] This Journal, **11**, 177.

[2] Ber. d. chem. Ges., **25**, 2255; and **26**, 2823, and 2829.

They have also shown that this reaction might be taken advantage of in the preparation of ethers, (alkyl oxides) simple and mixed. In fact by the action of alcohols upon the sulphonic ethers at somewhat elevated temperatures they succeeded in preparing several ethers which, hitherto, by the usual methods, had only been prepared with difficulty and in small quantities. In order to compare accurately the conduct of the carbonic and sulphonic acids in regard to the reaction of their ethereal salts towards absolute alcohol, small weighed quantities of ethyl benzoate and ethyl benzenesulphonate were heated in sealed tubes in boiling water for one-half hour with 50 times the required quantity of absolute ethyl alcohol. In this time 45 per cent. of the ethyl benzenesulphonate were saponified while of the ethyl benzoate only 3 per cent. were saponified. It was with the view of making a thorough study of the kinetics of the saponification of the sulphonic ethers by means of alcohol that this investigation was undertaken. The first preliminary experiments were made by Mr. H. H. Hill, with results not altogether satisfactory, owing to impure material. A careful study of the methods employed in making the sulphonic ethers has put into our hands a better material. Nevertheless our studies along this line are by no means complete. The results, however, are believed to be accurate and of sufficient interest to warrant this preliminary notice.

The following ethereal salts were selected for the investigation: Ethyl benzenesulphonate, ethyl (*p*)-chlorbenzenesulphonate, ethyl (*p*)-brombenzenesulphonate, and ethyl (*p*)-iodobenzenesulphonate. Of these the first three are known and require no word of description. Perhaps a word regarding the last one of which no mention is made in the literature may not be out of place in this connection.

Ethyl (p)-Iodobenzenesulphonate.—This compound was prepared by treating (*p*)-iodobenzenesulphonchloride dissolved in absolute ether with sodium ethylate. By recrystallization from ether it was obtained in fine, four-sided, transparent prisms, which were found to melt at 51° C. (uncor.). It was without odor, insoluble in cold water, slightly soluble in hot, and very easily soluble in alcohols and ether.

Action of Different Alcohols upon Sulphonic Ethers at Ordinary Temperature.

The first experiments along this line were tried with ethyl benzenesulphonate and several alcohols, each in various proportions, for thirty days at ordinary temperature. Small quantities of the ether, about 0.25 gram, were placed in a tightly-stoppered flask with 1, 10, 50, 100, 500, and 1,000 times the quantity of the alcohol required for its saponification. These experiments were concluded at the end of thirty days, and the extent of the saponification determined by titration with $\frac{1}{10}$ N. caustic potash. In the following table, No. 1, are to be found the results of these experiments:

TABLE I.

Proportion of alcohol to ether.

Kind of alcohol.	1:1	10:1	50:1	100:1	500:1	1000:1	
Methyl...	1.61	20.38	26.85	25.65	23.03	23.04	per cent. saponification.
Ethyl	2.04	17.52	19.20	18.47	17.31	16.30	" " "
N-Propyl .	3.81	15.55	16.94	17.65	17.36	....	" " "
Iso-propyl	1.86	13.45	19.36	20.30	19.72	19.88	" " "

These results show first that the saponification takes place readily even at ordinary temperatures; and secondly, that the rate of saponification is very nearly the same for all of the alcohols employed except for methyl alcohol, for which it is decidedly greater; and, thirdly, that the maximum of saponification is reached with from 50 to 100 times the required quantity of the several alcohols employed. The fact that larger quantities than these cause a falling off in the amount of saponification in a given time would seem to indicate that with very large quantities of alcohol the saponification would be altogether checked, for the reason probably that by mass action the large quantities of alcohol would tend to reform the ethers as rapidly as it was saponified.

Similar results, with two alcohols, were obtained with ethyl (*p*)-brombenzenesulphonate as shown in the following table, No. II:

TABLE II.

Proportion of alcohol to ether.

Kind of alcohol.	1:1	10:1	50:1	100:1	500:1	1000:1	
Methyl...	1.60	42.15	50.38	49.28	45.00	44.73	per cent. saponification.
Ethyl	3.24	35.00	40.27	37.86	36.64	38.00?	" " "

In this case it is also seen that a maximum of saponifica-

tion is reached with 50 times the required quantity of the alcohol; and also the same difference is observable in the action of the two alcohols, the methyl being decidedly the more active.

In order to compare the rates of saponification of the halogen ethers with that of the ethyl benzenesulphonate, small, weighed quantities of the several ethers were allowed to stand in tightly-stoppered flasks for twenty-two days, at ordinary temperature, with 50 times the required quantity of ethyl and methyl alcohol. The results are to be found in the following table, No. III:

TABLE III.

Kind of alcohol.	Ethyl benzenesulphonate.	Chlor-ether.	Brom-ether.	Iodo-ether.	
Methyl....	13.11	28.26	31.05	28.65	per cent. saponified.
Ethyl.....	8.78	21.05	21.34	20.44	" " "

From these results it will be easily seen that the halogens exert a very great influence on the rate of saponification; and that, curiously, each of the halogens increases the rate of saponification to the same extent; and here again it will be observed that in every case the methyl alcohol acts more strongly than the ethyl.

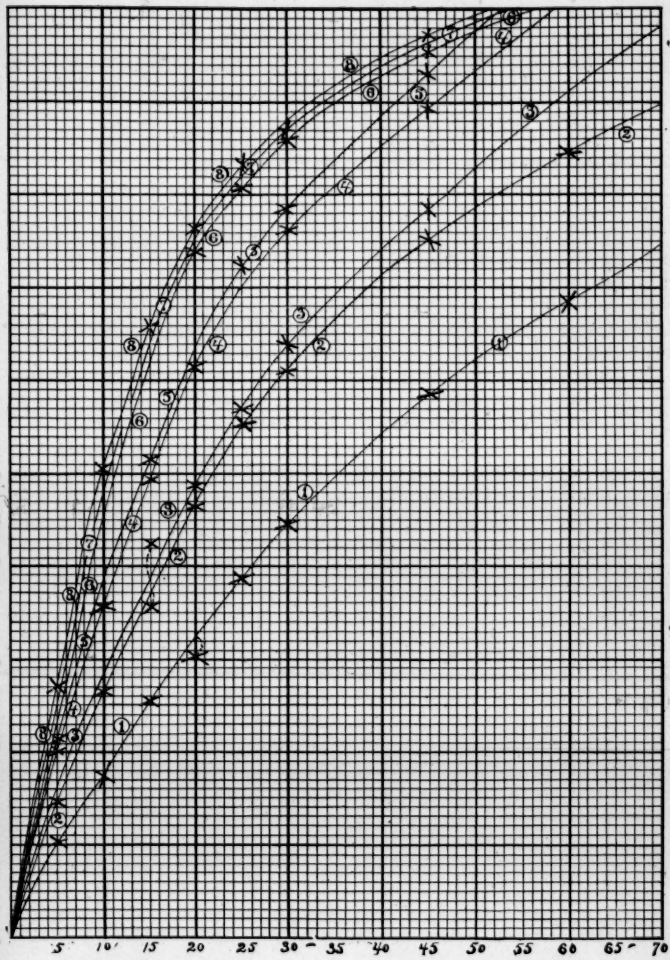
On the Action of Methyl and Ethyl Alcohols upon the Sulphonic Ethers at 100° C.

It was also deemed expedient to try the effect of higher temperatures upon the saponification of these ethers. Accordingly, small, weighed quantities of each of the above-mentioned ethers were heated in small sealed tubes in boiling water with 50 times the required quantity of alcohol. Ethyl and methyl alcohols were used in the experiments. Experiments with each ether were tried for five, ten, fifteen, twenty, twenty-five, thirty, and forty-five minutes, and one hour, except when otherwise indicated in tables Nos. IV, V, VI, and VII, in which are to be found the results of these experiments. These results have also been plotted as curves, (see p. 295) with the several intervals of time for abscissae and the percentages of saponification as ordinates.

TABLE IV.

Ethyl benzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.	1 hour.	
Methyl.	14.13	26.45	35.66?	46.67	55.12	60.87	75.52	84.5	per cent. sapon.
Ethyl ..	9.26	17.59	25.46	30.87?	38.31	44.52	58.43	68.65	" "



1. Ethyl sulphobenzoate with ethyl alcohol.
2. Ethyl sulphobenzoate with methyl alcohol.
3. Chlor-ether with ethyl alcohol.
4. Iodo-ether with ethyl alcohol.
5. Brom-ether with ethyl alcohol.
6. Chlor-ether with methyl alcohol.
7. Brom-ether with methyl alcohol.
8. Iodo-ether with methyl alcohol.

TABLE V.

Ethyl (p)-Chlorbenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.	
Methyl.	25.06?	....	57.15?	73.91	81.04	85.82	95.23	per cent. sapon.
Ethyl ..	23.00?	37.91?	42.68	58.37	66.73	73.09	88.01	" "

TABLE VI.

Ethyl (p)-Brombenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.	
Methyl.	27.58	....	64.95	....	....	86.89	100.00?	per cent. sapon.
Ethyl ..	20.87	....	51.16	....	....	78.3	93.16	" "

TABLE VII.

Ethyl (p)-Iodobenzenesulphonate.

Kind of alcohol.	5 min.	10 min.	15 min.	20 min.	25 min.	30 min.	45 min.	
Methyl.	27.13	50.60	65.27	76.46	83.46	96.47?	96.98	per cent. sapon.
Ethyl ..	20.00	35.54	49.56	61.54	72.10?	76.41	89.63	" "

The effect of raising the temperature is to greatly increase the saponification; otherwise practically the same relations hold for the reactions that were observed for lower temperatures; that is, the saponifying effect of methyl alcohol is greater than that of ethyl; and the ethers of the halogen benzenesulphonic acids are more easily saponified than that of ethyl benzenesulphonate; and except for the ethyl (*p*)-chlorbenzenesulphonate with ethyl alcohol, each of the halogens seems to accelerate the saponification to the same degree.

A consideration of the curves on p. 295, brings out these points very clearly. The curves for the halogen ethers saponified by methyl alcohol are sufficiently near to each other and so nearly concentric as to be considered identical. The curves representing the saponification of the halogen ethers by ethyl alcohol are also in the case of the iodo and the brom-ether sufficiently near together to be considered the same, whereas the curve for the chlor-ether, diverges somewhat from both of the above. Lastly, the curves representing the saponification of the benzenesulphonic ether with ethyl and methyl alcohol are clearly divergent from those of the halogen ethers and also from each other.

Conclusions.

From the experiments above described the following conclusions may be drawn:

(1) The ethers of the sulphonic acids are easily saponified by alcohols.

(2) A rise of temperature causes a great increase in the rate of saponification.

(3) Of the alcohols tried, methyl alcohol is undoubtedly the most powerful in its action, while the other alcohols seem to be about the same in their action.

(4) The replacement of hydrogen by a halogen in the sulphonic acid renders the ethereal salts of the substituted acid more easy to saponify.

(5) Except in one case, no difference, save such as could be brought within the limits of experimental error, was observable in the rate of saponification of the ethers of the halogen sulphonic acids, thereby indicating these three halogens to be alike in their capacity to accelerate the saponification of a sulphonic ether.

STATE COLLEGE OF KENTUCKY, LEXINGTON,
February, 1895.

Contributions from the Chemical Laboratory of Harvard College.

LXXXVI.—ON THE CUPRIAMMONIUM DOUBLE SALTS.

THIRD PAPER.[1]

BY THEODORE WILLIAM RICHARDS AND GEORGE OENSLAGER.

The work already done upon the double salts of cupriammonium[2] suggested the possibility of obtaining compounds of fluorine and iodine similar to those of chlorine and bromine.

Many attempts were made to prepare cupriammonium aceto-fluoride, $Cu(NH_3)_2FC_2H_3O_2$, with invariable failure. The methods and the proportions of the various reagents were varied in every possible way; but nothing could be obtained beside cupriammonium acetate and ammonium fluoride. Cupriammonium fluoride itself is very difficult to prepare, because of its solubility; and it is not strange that the double salt should be more so. It will be remembered, moreover, that while cupriammonium acetobromide is very easily

[1] Presented to the American Academy of Arts and Science, June 9, 1894.

[2] Richards and Shaw: this Journal, **15**, 642; also Richards and Whitridge: this Journal, **17**, 145.

obtained, the normal acetochloride is made with great difficulty by ordinary crystallization. We should expect the fluorine compound to be even less easily formed. Because of these continued failures, the work with fluorine was discontinued.

The investigation of the compounds of iodine proved much more fruitful, yielding the following new substances:

(1) $Cu(NH_3)_3IC_2H_3O_2$;

(2) $7Cu(NH_3)_2(C_2H_3O_2)_2 + Cu(NH_3)_2IC_2H_3O_2$;

(3) $Cu_3(NH_3)_{10}I_4$;

(4) $2Cu(C_2H_3O_2)_2NH_4C_2H_3O_2.H_2O$;

besides confirming the work of Foerster[1] on the following substances:

(5) $Cu(NH_3)_2(C_2H_3O_2)_2$.

(6) $Cu(NH_3)_2(C_2H_3O_2)_2 2\frac{1}{2}H_2O$.

(1) Ammon-Cupriammonium Acetoiodide, $Cu(NH_3)_3IC_2H_3O_2$.

In preliminary experiments the following method was used for preparing this compound: 4 grams of finely powdered cupric acetate were stirred with a mixture of 10 cc. of water, 20 cc. of alcohol, and 8 cc. of glacial acetic acid. Ammonia gas was then passed into the mixture until all the cupric acetate was dissolved and the color of the solution had become a deep blue. After the addition of 3.5 grams of ammonic iodide, the solution was set aside to crystallize and, in about six hours, large deep-blue, monoclinic plates having a six-sided outline, separated out. These crystals were washed with alcohol, and then dried between filter-papers as rapidly as possible. The salt thus prepared is usually not very pure, hence subsequently more alcohol was used in the preparation, with better success. Even yet, however, there was room for improvement.

After many systematic experiments which need not be detailed, the following method was found to yield excellent results: 12 grams of cupric acetate were dissolved in 50 cc. of ammonia-water (sp. gr. = 0.90) in a flask. After cooling, 30 cc. of aqueous acetic acid (57-per cent.) were added to the solution, then 6 grams of ammonic iodide, and finally 50 cc. of alcohol. Upon boiling on the water-bath, the mixture

[1] Ber. d. chem. Ges., **25**, 3412.

yielded a clear, deep-blue solution, which deposited crystals of ammon-cupriammonium acetoiodide upon slow evaporation in the air. The first very small crop of crystals deposited upon cooling was not analyzed. The second served for analysis IV below, and the third crop for analyses V and VIII. The substance used in analyses I, II, III, VI, and VII was prepared by earlier, less satisfactory, methods; it was undoubtedly the same substance, however.

Ammon-cupriammonium acetoiodide consists of brilliant, deep-blue, crystalline, monoclinic plates. It is not very permanent in the air, although much more so than its chlorine and bromine analogues. Upon exposure for a long time, the crystals become dull and dark in color, and the substance slowly loses in weight. Water at once decomposes it, some of the copper going into solution, and the rest remaining as a basic precipitate. Acids set iodine free, and precipitate cuprous iodide, as might be expected. The only unexpected property of the salt is the fact that it contains no crystal-water, thus not maintaining a strict analogy with the chlorine and bromine compounds, $Cu(NH_3)_3ClC_2H_3O_2.H_2O$ and $Cu(NH_3)_3BrC_2H_3O_2.H_2O$. The reason for this anomaly remains obscure.

The ammonia present in the compound was determined by distillation with pure potash or soda, the distillate being titrated with standard acid. It is convenient to prepare the alkali for this purpose directly from metallic sodium or from sodium-amalgam, thus avoiding the complications in the subsequent proceedings introduced by the usual impurity of chlorine in commercial alkali. The residue in the distilling flask, after the ammonia had been expelled, was filtered, and to the filtrate was added a little sulphurous acid to reduce any iodate which might have been formed. Argentic nitrate was then added, and afterwards the argentic oxide and sulphite were dissolved by nitric acid, the argentic iodide being collected and weighed upon a Gooch crucible. In analysis IV the alkali was nearly neutralized, and in analysis V the solution was just acidified by pure nitric acid before the precipitation. In every case enough nitric acid was added after the precipitation to insure the solution of all but argentic iodide, and the agreement of the results is sufficiently satisfactory. The

copper was determined by electrolysis of the cupric sulphate obtained from the precipitated cupric oxide, which contained no trace of iodine[1]; and the acetic acid was determined by combustion.

Analyses of $Cu(NH_3)_3IC_2H_3O_2$:

I. 0.2591 gram of the substance, on distillation with potash, required 25.34 cc. of decinormal acid for neutralization, gave, on electrolysis, 0.0545 gram of copper, and yielded 0.2042 gram of argentic iodide.

II. 0.2524 gram of the substance required 25.05 cc. of decinormal acid, and gave 0.0527 gram of copper.

III. 0.2322 gram of the substance required 23.25 cc. of decinormal acid.

IV. 0.3960 gram of the substance gave 0.3109 gram of argentic iodide.

V. 0.2559 gram of the substance gave 0.2004 gram of argentic iodide.

VI. 0.3211 gram of the substance gave, on combustion, 0.0931 gram of carbon dioxide.

VII. 0.2946 gram of the substance gave, on combustion, 0.0864 gram of carbon dioxide.

VIII. 0.3062 gram of the substance gave, on combustion, 0.0907 gram of carbon dioxide.

No.	Copper.	Ammonia.	Iodine.	Acetic acid.
I.	21.03	16.73	42.58	....
II.	20.88	16.95	....	....
III.	....	17.10	....	....
IV.	....	....	42.41	....
V.	....	....	42.31	....
VI.	....	....	....	19.46
VII.	....	....	....	19.67
VIII.	....	....	....	19.86
Average,	20.96	16.93	42.43	19.66

	Calculated for $Cu(NH_3)_3IC_2H_3O_2$.	Found.
Copper	21.15	20.96
Ammonia	17.03	16.93
Iodine	42.19	42.43
Acetic acid	19.63	19.66
	100.00	99.98

[1] Tested in analyses IV and V.

(2) Octo-Cupriammonium Monoiodide Acetate.

On allowing the mother-liquor remaining from the first method of preparing ammon-cupriammonium acetoiodide to stand for a long time, large coal-black hexagonal crystals of unknown composition were deposited. Mixed with these were large blue crystals, which were separated mechanically from the black ones, and analyzed. The analysis corresponded closely with the formula $7Cu(NH_3)_3(C_2H_3O_2)_2 + Cu(NH_3)_3IC_2H_3O_2$, the complexity of which led to the suspicion that the crystals were a mixture instead of a definite compound. Nevertheless, upon testing, the smallest as well as the largest crystals were found to contain iodine. In external appearance the crystals, which were usually at least half a centimeter in length, resembled those of cupriammonium acetate. An attempt was made to measure the angles of the crystals of each substance, but the faces were so covered with striations that the result was only partially satisfactory. For cupriammonium acetate the chief prism angle was about 70°, while for the complicated salt under discussion it was over 71° 30′. Even allowing a considerable margin for possible error, it would appear that the complicated salt must be a definite compound, and not merely cupriammonium acetate containing occluded cupric acetate and ammonic iodide. Another evidence of the probable definiteness of the salt is to be found in the fact that Richards and Moulton, in a paper yet to be published, have proof of the existence of a similar compound containing aniline and bromine instead of ammonia and iodine. The compound has no unexpected properties, and was analyzed in the usual fashion.

Analyses of $Cu_8(NH_3)_{16}I(C_2H_3O_2)_{15}$.

I. 0.2545 gram of the substance, distilled with soda, required 22.68 cc. of decinormal acid, gave 0.0333 gram of argentic iodide, and, on electrolysis, yielded 0.0707 gram of copper.

II. 0.2120 gram of the substance required 18.52 cc. of decinormal acid.

III. 0.2419 gram of another sample of the substance required 21.23 cc. of acid, and gave 0.0331 gram of argentic iodide and 0.0680 gram of copper.

No.	Copper.	Ammonia.	Iodine.
I.	27.78	15.25	7.07
II.	....	14.93	....
III.	28.11	14.99	7.39
	27.95	15.05	7.23

	Calculated for $Cu_8(NH_3)_{16}I(C_2H_3O_2)_{15}$.	Found.
Copper	28.35	27.95
Ammonia	15.22	15.05
Iodine	7.07	7.23
Acetic acid (by difference)	49.36	49.77
	100.00	100.00

Every effort to make the normal cupriammonium acetoiodide, $Cu(NH_3)_2IC_2H_3O_2$, free from cupriammonium acetate was unsuccessful; when so much of the ammonia has evaporated that the salt $Cu(NH_3)_2IC_2H_3O_2$ ceases to form, the singular double salt which has just been described always makes its appearance.

(3) TETRAMMON-TRICUPRIAMMONIUM IODIDE, $3Cu(NH_3)_2I_2+4NH_3=Cu_3I_4(NH_3)_{10}$.

This interesting substance may be prepared by a method very closely resembling that used for preparing ammoncupriammonium acetoiodide. If 8 grams instead of 12 grams of cupric acetate be used with 50 cc. each of ammonia and of alcohol, 30 cc. of acetic acid, and 6 grams of ammonic iodide, curious black crystals resembling irregular triangular pyramids make their appearance in the first place.

The new substance is somewhat similar in aspect to the corresponding bromine compound[1] although less brilliant. The crystalline faces are so singularly marked and striated that an accurate crystallographic study would not be feasible. They possess a distinct bronze lustre which soon disappears, owing to superficial decomposition. Upon exposure to the air the substance loses ammonia and iodine, finally leaving cuprous iodide. It is decomposed by water. Heated in aqueous or alcoholic ammonia it dissolves, forming a deep-blue solution which upon cooling deposits bright-blue needles. These remain to be investigated.

[1] Richards and Shaw: this Journal, **15**, 651.

From the mother-liquors decanted from the black crystals may be obtained, at first, $Cu(NH_3)_3IC_2H_3O_2$, and, finally, a mixture of $Cu_6(NH_3)_{18}I(C_2H_3O_2)_{11}$ with the coal-black, six-sided crystals already mentioned.[1] These latter crystals are very different in appearance from $Cu_3(NH_3)_{10}I_6$; they will be investigated in the future.

Analyses of $Cu_3(NH_3)_{10}I_6$.

I. 0.2049 gram of the substance yielded ammonia requiring 18.22 cc. of decinormal acid for neutralization, and 0.0352 gram of copper, on electrolysis.

II. 0.2315 gram of the substance required 20.24 cc. of acid and gave 0.0385 gram of copper and 0.2901 gram of argentic iodide.

III. 0.2302 gram of the substance required 20.36 cc. of acid and gave 0.2872 gram of argentic iodide.

IV. 0.2307 gram of the substance required 20.35 cc. of acid.

V. 0.2150 gram of the substance gave 0.0367 gram of copper, on electrolysis.

No.	Copper.	Ammonia.	Iodine.
I.	17.17	15.19	....
II.	16.63	14.94	67.41
III.	....	15.11	67.84
IV.	....	15.07	....
V.	17.07	....	....
	16.96	15.08	67.62

	Calculated for $Cu_3(NH_3)_{10}I_6$.	Found.
Copper	17.00	16.96
Ammonia	15.20	15.08
Iodine	67.80	67.62
	100.00	99.66

(4) Ammonic Dicupric Acetate, $NH_4Cu_2(C_2H_3O_2)_4H_2O$.

Since compounds containing 3 molecules of ammonia, 1 of acetic acid, and 1 atom of chlorine, bromine, or iodine had been proved to exist, it became a matter of interest to discover if it were possible to prepare a salt of the com-

[1] Page 301.

position, $Cu(NH_3)_3(C_2H_3O_2)$, in which the halogen is replaced by acetic acid. Many unsuccessful attempts were made to obtain this compound. In the course of these experiments, however, a new double salt of cupric and ammonic acetates was discovered. 4 grams of cupric acetate, 6 grams of glacial acetic acid, and 20 cc. of alcohol were mixed together, and ammonia-gas was passed into the mixture until the green color just turned to blue. The solution became hot from the absorption of the ammonia, and the cupric acetate dissolved readily. After standing a few hours, many small, bluish-green crystals were deposited, which had the composition given below. The crystals are soluble in water without decomposition, and are fairly permanent in the air.

Analyses of $Cu_2(NH_4)(C_2H_3O_2)_5H_2O$.

I. 0.2586 gram of the substance yielded an amount of ammonia requiring 5.49 cc. of decinormal acid, and, on electrolysis, gave 0.0717 gram of copper.

II. 0.4303 gram of the substance required 9.40 cc. of acid.

III. 0.2525 gram of the substance gave 0.0703 gram of copper.

IV. 0.2604 gram of the substance required 5.52 cc. of acid and gave 0.0725 gram of copper.

V. 0.3080 gram of the substance gave, on combustion, 0.2970 gram of carbon dioxide.

No.	Copper.	Ammonium.	Acetic acid. $C_2H_3O_2$.
I.	27.73	3.84	....
II.	....	3.96	....
III.	27.84	....	....
IV.	27.84	3.84	....
V.	....	....	64.67
Average	27.80	3.88	64.67

	Calculated for $Cu_2NH_4(C_2H_3O_2)_5H_2O$.	Found.
Copper	27.75	27.80
Ammonium	3.94	3.88
Acetic acid	64.38	64.67
Water (by diff.)	3.93	3.65
	100.00	100.00

(5) AND (6) CUPRIAMMONIUM ACETATE.

This salt, discovered by Foerster,[1] may be prepared in an anhydrous condition by allowing an alcoholic solution of cupric acetate to evaporate in the air. Two determinations of the copper present in the blue crystals showed respectively 29.41 and 29.32 per cent., the theoretical being 29.48. The ammonia was found to be 15.68, instead of the theoretical amount 15.82 per cent., corresponding to the formula, $Cu(NH_3)_2C_2H_3O_2$.

The crystallized salt, containing $2\frac{1}{2}$ molecules of crystal water, also discovered by Foerster, was prepared in blue, feathery crystals by the evaporation of aqueous ammoniacal cupric acetate. Analysis showed the percentage of copper present to be 24.23 instead of 24.38, and the ammonia to be 13.02 instead of 13.08 per cent. The theoretical values were calculated for the formula $Cu(NH_3)_2(C_2H_3O_2)_2 2\frac{1}{2}H_2O$.

All of these compounds, as well as many similar obtained from other acids and the substituted ammonias, will be further studied at this laboratory in the near future.

CAMBRIDGE, MASS.

BASSWOOD-OIL.

BY F. G. WIECHMANN.

As, in the literature available, no mention could be found of an oil in basswood (*Tilia Americana*), which the writer recently noticed and extracted, a brief record of the results obtained by an examination of this substance may be of interest.

Two samples of basswood were examined. Both came from the same region, Saginaw, Michigan. They were cut into boards about half an inch in thickness, and about 10 inches in breadth.

Sample No. 1 was sound wood; sample No. 2 presented a peculiar stained appearance and emitted a very strong and disagreeable odor strongly resembling that of rancid butter. On inquiry it was learned that this wood had been kept lying in water for a considerable length of time, and it was evident that some constituent of the wood was undergoing decomposition, which resulted in the formation of some volatile fatty acids.

[1] *Loc. cit.*

In both instances the sample was prepared for analysis by use of a rasp, a fine wood-powder resulting. In the sound wood the whole breadth of the board was evenly worked over; in the other case care was taken to secure the wood-powder principally from the "stained" portions. The oil was extracted in a Soxhlet extraction-tube. 70 grams of wood-powder were used in both instances, and extraction was accomplished by the use of pure ether; the time for extraction was two hours for each charge in the tube. The following results were obtained by examination of the oils, the ether having, of course, been previously removed:

	No. 1.	No. 2.
Yield (expressed in percentage of weight of wood-powder used)	5.24	3.72 3.70 3.68
Specific gravity $\frac{15^\circ}{15}$ C	0.938	—
Congeals at	−10° C.	+5° C.
Saponification-equivalent	315	Could not be determined; ranged from 152 to 77 inside of a few hours.
Iodine-absorption	111	60
Color	Olive-brown.	Dark-brown.
Heydenreich's reaction	Yellow and red-brown.	Yellow and red-brown.

Examining the properties of the vegetable oils mentioned in Allen's Commercial Organic Analysis (Vol. II, 2nd Edition), it appears that in some respects basswood-oil resembles cottonseed-oil. The following data on cottonseed-oil are given by Allen:

	Cottonseed-oil.	Basswood-oil.
Specific gravity at 15° C	0.928 0.930	0.938
Solidifying-point	1°–10°C.	−10°C.
Iodine-absorption	105–109	111
Saponification-equivalent	285–294	315[1]
Heydenreich's reaction	Reddish-brown.	Yellow and red-brown.

To examine into the nature of the decomposition which the oil obtained from basswood, No. 2, was undergoing, an ether-extract of this oil was saponifed by a potassium-hydrate solu-

[1] This high saponification-equivalent is possibly due to the presence of a small amount of resin which was determined in the oil.

tion, twenty hours in all being allowed for the reaction. Water was then added and the mixture placed in a separating-funnel. In this manner a soap solution and an ether solution were obtained. The treatment to which these solutions were subjected, and the data which were secured, are noted in the following scheme:

Soap Solution.	*Ether Solution.*
Added sulphuric acid till strongly acid; heated on water-bath for forty-five minutes; filtered while hot and washed with boiling water until reaction was no longer acid.	Evaporated to dryness on water-bath; residue oily in character. Hydrocarbons or unsaponified oil. Weight = 0.1616 gr. Congeals at + 2° C.
Residue in Filter.	*Filtrate.*	*Residual Solution.*
Dissolved by alcohol-ether (1:1) and evaporated carefully to dryness. Insoluble fatty acids = 0.4951 gr. Specific gravity = 0.898. Congeals at + 5.5° C. Mean combining weight = 342.	Distilled by live steam passing through for two hours. *Distillate.* Neutralized with sodium hydrate (phenolphthalein as indicator); evaporated to dryness and constant weight at 100° C. Volatile fatty acids = 0.1379. Mean combining weight = 92.	Neutralized with potassium hydrate (phenolphthalein as indicator); evaporated to dryness on water-bath; extracted residue with ether-alcohol; evaporated to a syrupy solution. Glycerol = 0.2235 gr. Responded to the acrolein and other tests for glycerol.

These results show that the oil is a glyceride which has suffered partial decomposition, originally induced, most probably, by the presence of mucilaginous or albuminous matter. The volatile fatty acids separated consisted, undoubtedly, in great measure, of butyric acid and its immediate allies.

In conclusion the writer would express his thanks to Messrs. Brainerd and Ziebolz for valuable assistance rendered in securing the analytical data.

COLUMBIA COLLEGE.

NOTE.

A Reagent to replace Hydrogen Sulphide in Qualitative Analysis.

Schiff and Tarugi[1] recommend the use of thiacetic acid as a reagent for the separation of the metals of the second group, thereby avoiding the disagreeable odor of hydrogen sulphide. The acid decomposes with hot hydrochloric acid, giving a very active, nascent hydrogen sulphide, which completely precipitates all the metals of this group. The reagent is made by dissolving 10 cc. of the pure acid in an excess of dilute ammonia, making about 30 cc. ammonium thiacetate solution, which is colored slightly yellow and possesses a weak odor of ammonium sulphide. To the solution to be tested, containing 0.5–1 gram of substance 1–2 cc. of the reagent are added; the solution is then heated to near boiling, but not to the boiling-point. On cooling, there is complete separation of the metals as sulphides. Bismuth, copper, stannous and stannic salts are partially precipitated in the cold, but completely on warming. Lead, mercury, platinum, and gold give red precipitates at first, which are charged to the sulphides on heating. Arsenites and arsenates are separated as the trisulphide. Cadmium is slightly soluble in the hot hydrochloric acid solution, but, on cooling, all of the sulphide is obtained. The chloride, bromide, and iodide of silver are converted into silver sulphide; ferric and chromic salts are instantly reduced to ferrous and chromous salts. Aluminum, manganese, nickel, cobalt, and zinc are not affected, but can be precipitated from an ammoniacal solution. The authors state that they have used the reagent with great satisfaction, and that it has given good results even in the hands of beginners. H. F.

[1] Ber. d. chem. Ges., **27**, 3437.